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Biological Monitoring of Toxic Trace Metals
Volume 1, Biological Monitoring and Surveillance

Dale W. Jenkins
Sarasota, FL

Prepared for

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BIOLOGICAL MONITORING OF TOXIC TRACE METALS
Volume 1. Biological Monitoring and Surveillance

by

Dale W. Jenkins
3028 Tanglewood Drive
Sarasota, Florida 33579

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Project Officer

John A. Santolucito
Exposure Assessment Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89114

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ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

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16. ABSTRACT

The needs and priorities in using biological accumulator organisms for monitoring toxic trace metals in plants and animals are analyzed. The toxic trace metals selected for study are antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, tin, and vanadium. Data on the toxicity to humans, abundance, production, use and emissions of trace elements are presented and sources and pathways to plants and animals listed.

Volume 1 of the two volumes evaluates available data for the purpose of selecting biological monitoring organisms to monitor the 14 selected toxic metals, and recommends various organisms for use in national and international monitoring systems and networks. This study is based on the data compilation in Volume 2.

Volume 2 brings together the majority of the significant data on bioaccumulation and bioconcentration of the 14 trace metals discussed, which are considered to be of most importance to man and his food organisms. This volume provides a concise reference of baseline data for delineating the background or "normal" levels of toxic trace metals as well as levels that occur under various pollutant conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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FOREWORD

Protection of the environment requires effective regulatory actions based on sound technical and scientific data. The data must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of exposure to specific pollutants in the environment requires a total systems approach that transcends the media of air, water, and land. The Environmental Monitoring Systems Laboratory at Las Vegas contributes to the formation and enhancement of a sound monitoring-data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

Volume 1 of the two volumes in this report evaluates available data for the purpose of selecting biological monitoring organisms to monitor 14 of the more important toxic metals, and recommends various organisms for use in national and international monitoring systems and networks. This study is based on the data compilation in volume two.

Volume 2 brings together the majority of the significant data on bioaccumulation and bioconcentration of 14 of the trace metals of most importance to man and his food organisms. This volume provides a concise reference of baseline data for delineating the background or "normal" levels of toxic trace metals as well as levels that occur under various pollutant conditions.

The report was complied primarily to aid those who are seeking the best biological samplers to use in a biological monitoring system or network, and will help to show environmental movement, pathways, and sinks for selected metals in relation to biological organisms. Further information concerning these volumes and biological monitoring network design may be obtained from the Exposure Assessment Division at the Environmental Monitoring Systems Laboratory.

Glenn Schweitzer
Director
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada

ABSTRACT

The needs and priorities in using biological accumulator organisms for monitoring toxic trace metals in plants and animals are analyzed. Monitoring objectives are: a) integrated exposure assessment monitoring, b) surveillance monitoring of the global, regional and local environments, and c) surveillance monitoring of food. The toxic trace metals selected for study are antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, tin and vanadium. Data on the toxicity to humans, abundance, production, use and emissions of trace elements are presented and sources and pathways to plants and animals listed. The highest priority needs are for biological monitoring of lead and cadmium, and the lower priority for mercury and arsenic.

This Volume 1 of two volumes includes analysis of the comprehensive data listed in Volume 2 on bioaccumulation and bioconcentrations of the 14 trace metals in plants and animals. Data on use of plants and animals for monitoring environmental gradients of the trace metals and on biomagnification of trace metals in food chains are analyzed.

It was found that decreases of metals in food chains, named here as biominification, were more important in the higher trophic levels from prey to predator. Exceptions were mercury and cadmium, which are bioaccumulated by organisms with age.

Biotransformation of elements and compounds is also considered. A large number of species of plants and animals with proven capability or potential for use as biological monitoring organisms are listed. Final selection was based on the needs, priorities and objectives for monitoring, and also on the degree of fit to eight criteria for selection. The organisms selected are human hair for monitoring man; rats, pigeons, domestic animals, food plants and crops, and mosses and lichens for monitoring the immediate environment; domestic animals, selected higher plants, especially food crops, mosses and lichens, and selected species of birds for monitoring the terrestrial environment; and marine algae and bivalve molluscs for monitoring the aquatic environment. Limited monitoring using fish, mainly for food surveillance, is recommended.

Global and national biological monitoring for integrated exposure assessment, and for environmental and food surveillance are reviwed. It is recommended that exposure monitoring networks be established to assess exposure to lead and also to cadmium of humans at highest risk, especially children in cities. Biological monitoring of man using human hair, and the immediate environment of man, using rats, pigeons, and mosses and lichens is recommended.

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SECTION I

INTRODUCTION

Man has been mining and using trace metals for over 5,000 years, beginning with the first use of copper. Since that time lead and many other metals have been used in ever-increasing quantities until presently many millions of tons of trace metals are mined and utilized each year.

Of the presently known 105 elements, 77 are metals or metalloids of which 52 are of economic importance. About twenty of these metals are toxic to man and other biological organisms, either in the elemental form or in various chemical compounds that vary widely in toxicity, absorption and retention. It is a paradox that trace metals such as chromium, cobalt, copper, manganese, zinc and perhaps vanadium are essential in trace amounts to many living organisms, but in higher concentrations can also be toxic or lethal.

Toxic trace metals are being released into the environment in ever-increasing quantities as man mines and uses more of the metals in different ways. This is especially true in the highly industrialized countries where some toxic trace metals have reached such levels in the environment that they are causing a stressed environment. Environmental stresses that cause hazards to the quality of life were studied by Battelle Memorial Institute (Korte 1974). Toxic metals presently rank second in importance in all environmental stresses studied. Forecasts of future environmental stresses show that toxic metals are considered to be the major candidate for first place as hazards to the quality of life.

Flow of these toxic trace metals through the environment results from mobilization by both natural and man-induced sources. Man has greatly increased the environmental flow of some of these metals and has helped increase their hazards especially in more recent years.

It is well known that some of these trace elements are direct hazards to the health and life of man if the levels are sufficiently high. There is uncertainty about the lower levels of trace metals that can be tolerated in the environment, especially over long periods of time, and whether they produce delayed intoxication or disease states. Also of importance are the contamination and toxicity effects on biological organisms which serve as food for man.

It is necessary to measure the levels of toxic trace metals in man and his immediate environment. It is also important to determine environmental levels with regard to critical sources and pathways to point out hazards and to provide required information for effectively reducing or eliminating hazardous sources. It is essential to analyze the levels of trace metals in the environment to monitor their changes and trends and to develop an early warning system.

MONITORING

Monitoring is a scientifically designed system of continuing measurements and observations. This implies repetitive measurement in time and space.

There are different methods of monitoring and many objectives. The types of monitoring involved in this report are defined as follows:

BIOLOGICAL MONITORING

Biological monitoring is the use of biological organisms (or their products) for systematic and continuing measurements and observations of the concentrations and/or effects of environmental pollutants. This type of monitoring is usually contrasted to strictly instrumental monitoring.

It is essential in developing monitoring systems to clearly delineate the major target or critical receptor, which is defined as that segment of the human population or of the environment that is most adversely affected by exposure to a pollutant.

A major reason for monitoring is to provide data required for strategic control of critical sources of pollutants. Critical sources are defined as those sources that are major contributors to exposure of the critical receptors. Other reasons for monitoring are to define the degree and kind of exposures of the critical receptors, the critical pathways and media and ultimate sinks of the pollutants. A coordinated systems approach to monitoring has been developed.

INTEGRATED EXPOSURE ASSESSMENT MONITORING

Integrated exposure assessment monitoring is "the coordination of environmental (air, water, land and crops) monitoring networks to collect systematically pollutant exposure data for a specific receptor -- usually man." (Behar et al. 1979).

In addition to integrated exposure assessment monitoring, relating critical receptors to critical sources, there is another valuable reason for monitoring. This is surveillance to determine background baselines of reference data in unpolluted areas of the world to permit making valid comparisons with contaminated or polluted impact areas. In making these measurements on a global or regional scale, there is the opportunity to find undiscovered "hot spots" and to discover how dispersion of the trace metals occurs. These baseline studies can also help define trends in the environmental levels of the trace elements.

SURVEILLANCE MONITORING

Surveillance monitoring is the repeated measurement of pollutants or their effects, for the purpose of detecting and measuring levels to establish temporal and/or spatial trends.

The National Pesticide Monitoring Program is an excellent example of surveillance monitoring to establish baselines, estimate trends, evaluate effectiveness of management and regulatory decisions, and support an early warning system for pesticide-caused environmental problems. Surveillance monitoring of pesticides and heavy metals in foods in the "Market Basket Survey" typifies this type of monitoring.

Monitoring of trace metals in man and his environment is expensive in time, materials and money. It is absolutely essential that monitoring measurements are clearly related to critical receptors and to critical sources. This is especially true since the problem of pollutant dispersion through various environmental media and pathways is usually highly complex and the impacts on a receptor may occur simultaneously due to exposure to various media. In order to assess the exposure of receptors to trace elements, a monitoring strategy should be capable of bridging the various media.

The EPA Las Vegas Laboratory has stated:

> "Since awareness of and impact on our ambient environment increases in direct proportion to the degree of environmental contamination, one may assume that the most efficient overall monitor for the environment is man, or some other living organism. Unfortunately we have not learned to use such monitoring systems efficiently." (Behar et al. 1979).

The major objective of this report is to assist in learning to use living organisms efficiently for biological monitoring of our environment. Comprehensive data on concentrations of selected toxic trace metals are presented in Volume 2. In this Volume 1 on biological monitoring, the problems, needs, priorities and selection and use of living organisms for monitoring are considered. A previous report, entitled "Toxic Trace Metals in Human and Other Mammalian Hair and Nails," (Jenkins 1979) was written to assist in using man as a biological monitoring organism, and/or for monitoring the levels of trace elements in man.

In order to define the trace metal problem, it is necessary to consider toxicity to man, abundance, production, use, emissions and geographic dispersion of the trace metals, and sources and pathways to biological organisms. In this study, the toxicity to man of the various selected toxic trace metals is briefly summarized. This includes effects from exposure to air as well as ingestion of food (biological organisms and their products) and water. The annual production of the toxic trace metals, their uses and their dispersion into the environment are reviewed. Since the major objective of this study is biological monitoring, only emissions inventories are summarized. Mass balance studies would be more valuable but the data needed were not available in usable form for each trace metal. This information is of value in defining the relative importance of each type of media for each pollutant and contributes to helping select specific monitoring organisms. Major sources and pathways to biological organisms are defined for each trace metal, and geographic dispersion and distribution are considered.

Data on accumulation levels of the trace metals in biological organisms have been tabulated for each group of organisms, and the results of using organisms for measuring environmental gradients of each trace metal have been reviewed and tabulated (based on data in Volume 2). All of this information was taken into consideration in making recommendations for potential biological monitoring organisms.

The actual selection of biological monitoring organisms for monitoring systems or networks, however, is based selection criteria. These criteria take into account more practical considerations, especially with regard to critical receptors and sources for exposure assessment monitoring, and the needs for global, regional (or national) and local surveillance monitoring.

Biological monitoring systems are recommended for a) man, b) the immediate environment and food of man (urban and rural), and c) the general environment (terrestrial, freshwater, and marine), including both remote unpolluted and heavily polluted impact areas. This includes a national (United States) network and a global or an international network.

SECTION II

DEFINITION OF BIOLOGICAL MONITORING REQUIREMENTS

In developing biological monitoring programs, it is necessary to define the pollutants of importance as health hazards and to select the most important for consideration. A series of toxic trace elements has been selected on the basis of specific criteria. To define the needs and relative priorities for monitoring these trace elements, data have been compiled on a) the toxic effects on man, and major exposure routes and pathways, b) relative abundance and concentrations, production, and use, c) emissions into the environment for each pollutant, and d) the major sources and pathways of each trace metal into plants and animals. This information was used not only for defining needs and relative priorities but also in helping select biological monitoring organisms.

SELECTION OF TOXIC TRACE METALS

There are about 20 trace elements that are toxic either in elemental form or in various chemical compounds to man and other biological organisms.

The Permanent Commission and International Association of Occupational Health has selected 30 metals in its handbook, "Toxicology of Metals, Vol. II," (Friberg 1977) based on both general environmental exposure and occupational exposure. Schroeder (1974) listed lead, antimony, beryllium, cadmium, arsenic, and mercury as toxic to living things, and tin, selenium, nickel, and eight other elements as slightly toxic to some life processes. He states that these toxic trace metals "are extremely important to the health of the public, being involved in at least half the deaths in the United States and much of the disabling diseases. Therefore, they are of public concern or should be, if we value our lives and our health." Schroeder (1974) also presented a law of nature, "The Toxicity of Relative Elemental Abundance. Elements which are highly abundant on the earth and in seawater are relatively non-toxic. Elements which are scarce on the earth and in seawater are usually toxic to living things. Toxicity of elements varies inversely with abundance."

The U.S. Environmental Protection Agency priority list of toxic substances includes cadmium, lead, mercury, and arsenic (Behar et al. 1979). The U.S. Food and Drug Administration currently lists mercury, lead, cadmium, arsenic, selenium, and zinc at the top of its priority list in its program of surveillance of toxic elements in food (Jelinek and Corneliussen 1977).

Trace metals listed by WHO (1972) as health hazards include arsenic, cadmium, lead and mercury, and potential health hazards include antimony, barium, beryllium, cobalt, manganese, nickel, selenium, tin and vanadium.

WHO (1976) established criteria that resulted in selection of some 70 chemicals and physical hazards. These criteria are:

1. Severity and frequency of observed or suspected adverse effects on human health.
2. Ubiquity and abundance of the agent in man's environment.
3. Persistence in the environment.
4. Environmental transformations or metabolic alterations.
5. Population exposed.

In initiating the present study in 1974 the following criteria were established for selection of the toxic trace elements: 1) The elements are toxic to man and/or his food organisms; 2) The elements are fairly common and widespread; 3) Exposure to elements is sufficient to cause a hazard or a potential hazard; 4) The elements are persistent in the environment; and 5) The elements are becoming of greater importance due to increased production and/or use.

On the basis of these criteria, 14 toxic trace elements were selected. These toxic metals or metalloids are as follows: antimony (Sb), arsenic (As), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), tin (Sn), and vanadium (V). Some of these, such as cadmium, lead and mercury, are of immediate importance while others such as beryllium, boron, vanadium and others do not appear to be of more than local importance at present. Also, additional trace elements such as manganese, zinc and others could have been considered for inclusion in the list.

These trace elements are often referred to as toxic heavy metals. While most are toxic, heavy, and metals, some such as beryllium are light (atomic number 9); some, such as arsenic and selenium are not metals but metalloids; and one element, boron, is not toxic to man and most animals. However, through popular usage and convenience, these trace elements are being referred to as trace metals.

TOXICITY OF TRACE METALS TO MAN

Certain chemical forms of these trace elements are dangerous to man and other biological organisms. Orally, antimony, arsenic, cadmium, copper, mercury, lead, selenium, and vanadium are toxic, and when injected, most of the metals are toxic. Some of the trace metals including arsenic, cadmium, lead, and mercury function as cumulative poisons. Some including beryllium, chromium, nickel, and arsenic are carcinogenic. Cadmium and lead, at the levels to which many people are exposed, cause life-shortening and frequent neurological disruption in experimental rats (Schroeder 1974). Copper, mercury, boron, tin, cobalt, and nickel below 1 ppm are toxic to certain species of plants.

Of the 20 metals with known degrees of toxicity to man, only five presently constitute an important threat to man. These are in order of importance: lead, cadmium, mercury, arsenic, and nickel. These were selected on the basis of toxicity to man, abundance, exposure of man, and history of causing problems. There are other metals of importance and some with higher toxicity, such as beryllium, but their abundance, geographic distribution or degree of exposure to man are limited.

Certain trace metals in low concentrations are highly toxic to plants and animals. For this reason they have been used as biocides or pesticides for control of unwanted or pest populations of organisms. Most of these trace metals are highly persistent and retain their toxicity for long periods of time. The most toxic, abundant, and persistent trace metals deserve special consideration for biological monitoring.

The different trace metals are highly selective in their effects on biological organisms. Some are extremely toxic in minute quantities to some organisms, but are accumulated in quantity with little observable effect in others. However, some metals are accumulated in special organs or tissues without effect, but if introduced into the bloodstream, they are highly toxic.

The effects on humans of each trace metal are briefly summarized, including effects of inhaled, ingested and contact exposures. Occupational exposure and data on absorption and accumulation of various compounds of each element are considered. A summarization of the toxicity of the element, more toxic compounds, and the hazards to man from food and air pollution is presented in Table 1.

Antimony

While antimony is a toxic trace element, it rarely has been reported to cause toxic effects in the general population. Antimony usually occurs in low levels in the environment, and there has been relatively little research on its toxic effects. Effects are known from occupational exposure and therapeutic use as well as from acute poisoning from food and beverages contaminated by containers made with antimony. Therapeutic use of antimony is for schistosomiasis, leishmaniasis, trypanosomiasis and ulcerative granuloma (WHO 1976a).

Occupational exposure from mining, smelting, formulating and finishing antimony products, and military uses has caused many toxic effects on the respiratory, cardiovascular, hepatic, cutaneous, reproductive and gastrointestinal systems. Pneumoconioses, respiratory tract inflammation, and cardiovascular alterations are the most common result. Skin effects such as blotches and pustules around sweat glands and gynecological disorders including abortions and premature deliveries also occur. It has not been shown to be carcinogenic (WHO 1976a).

Antimony halides are highly irritating and toxic (WHO 1976a). Stibnine (SbH_3) is toxic and attacks the circulatory and the central nervous system (Friberg 1977).

TABLE 1. TOXICITY OF SELECTED TRACE ELEMENTS TO HUMANS

	Toxicity of Element to Man	Most Toxic Compounds	Food Hazard	Air Pollution Hazard
Antimony	Toxic	halides and stibnine	(L)	low potential hazard
Arsenic	S	As_2O_3, arsine	hazard	hazard
Beryllium	Toxic	all	low	potential hazard
Boron	Low	borane	none	unknown
Cadmium	Toxic	all	hazard (L)	hazard
Chromium	S	hexavalent Cr	low	none
Cobalt	Low	---	hazard	none
Copper	Low	---		none
Lead	Toxic	all esp. tetraethyl Pb	hazard (L)	hazard
Mercury	Toxic	methyl Hg alkyl Hg	hazard	hazard
Nickel	S	nickel carbonyl	low	hazard
Selenium	Toxic	---	hazard	none
Tin	S	triethyltin tetraethyltin	(L)	none
Vanadium	Low	---	none	none

S - specific compounds toxic or highly toxic, but element moderate to low toxicity.
(L) - leaching from container contaminates food.

Arsenic

Arsenic is highly toxic in the trivalent form. Ingestion gives rise to abdominal pain and vomiting, inflammation of the gastrointestinal tract, peripheral neuritis, and exfoliative dermatitis. Chronic poisoning results in loss of appetite and weight, diarrhea alternating with constipation, gastrointestinal disturbances, peripheral neuritis, conjuctivitis, hyperkeratinosis and melanosis of the skin and sometimes skin cancer (WHO 1972).

The fatal oral dose of trivalent arsenic for man is 70 to 180 mg. Elemental and pentavalent arsenic is much less toxic. There is some evidence of adaptation to arsenic. Arsenic trioxide exposure in smelter workers resulted in dermatitis, perforated nasal septa, pharyngitis, peripheral neuritis and conjuctivitis. Arsenic may produce skin cancer and angiosarcoma of the liver (Friberg 1977).

Arsenic exposure or poisoning results in increased As levels in hair and nails which can be used to monitor humans and other mammals. Arsenic is also used as a therapeutic drug.

Beryllium

Beryllium compounds are highly toxic to man when inhaled. This results in acute chemical pneumonitis and chronic pulmonary granulomatosis (berylliosis). Chronic berylliosis eventually involves the adrenals, liver, kidney and heart. Some beryllium compounds can cause malignancies in experimental animals, but epidemiological studies have not shown a relationship between Be and human cancer. Beryllium compounds are not known to cause mutagenic or teratogenic effects. Beryllium compounds are not readily absorbed from the gastrointestinal tract or skin. Trace amounts in the blood tend to accumulate on a short-term basis in the liver and on a long-term basis in bone. Beryllium compounds cause allergic dermatitis with edematous lesions. (Oak Ridge Nat. Lab. 1978).

Most beryllium cases are occupational but there are neighborhood cases as well in the vicinity of Be extraction plants. Most cases have resulted from inhalation of aerosols of soluble Be compounds, typically fluoride. There have been some fatalities but recovery is usual after several weeks or months. Diagnosis of the lung disease is difficult, and Be in urine, blood or pulmonary specimens helps to establish exposure, but concentrations have no relation to the severity of the disease (Friberg 1977).

Boron

Boron has quite low toxicity to human beings in the elemental state and most compounds. However, boranes are highly toxic, and inhalation of borane vapors produces severe physical discomfort. Boranes have a characteristic odor similar to chocolate but distinctly disagreeable. Boron oxide is moderately toxic via ingestion, inhalation and skin-absorption (Oak Ridge Nat. Lab. 1977). Three grams of ingested boric acid per day did not produce toxic symptoms in man. Cattle have consumed 20 g of borax per day with no toxic symptoms (McKee and Wolf 1963). Boron is toxic to plants, and some species are damaged at 1.5 ppm in irrigation water.

Cadmium

Cadmium is a highly toxic element with no known useful biological function. It is thought to have been the cause of itai-itai disease in Japan in about 1950. It accumulates in the kidney cortex where it causes renal tubular dysfunction. Pulmonary edema and chronic emphysema are caused, and increased mortality due to total malignancies, lung cancer, and prostatic cancer have been shown in smelter workers. Cadmium causes hypertension in laboratory animals after prolonged exposure to low levels. Cd as a cause of osteomalacia is presently debated (Oak Ridge Nat. Lab. 1975).

Cadmium appears to be toxic in all forms and concentrations, due primarily to its ability to replace zinc and other essential trace metals from biologically important metallo-organic compounds (Oak Ridge Nat. Lab. 1975).

Cadmium is toxic to man, and acute poisoning can result from inhalation. Ingestion of cadmium through food is the most important method of exposure. Continued low-dose exposure to cadmium in foods is of great concern because of the long biological half-life of cadmium, 20 to 40 years, which permits substantial accumulation in the body. Also, the toxic potential of occasionally high cadmium exposures may be magnified because cadmium is not readily eliminated from the body (Friberg 1977).

Chromium

Chromium in the common trivalent form has relatively low toxicity. It is an essential trace element for many organisms. Hexavalent chromium is more toxic because of its oxidizing potential and its easy permeation of biologic membranes. It is irritating to the respiratory tract and produces ulceration and perforation of the nasal septum. Of greater significance is the production of lung cancer. A high incidence of bronchogenic carcinoma has been found in persons occupationally exposed. Acute systemic poisoning causes tubular necrosis of the kidney. Cutaneous injury from Cr includes scars, corrosive ulcers, non-ulcerative contact dermatitis and allergic effects, such as eczematous and noneczematous contact dermatitis (Friberg 1977).

No harmful effects on the health of man or animals are known to have resulted from the presence of chromium in the ambient air or in public drinking water at current concentrations. Relatively little is known about the influence of chromium on ecological systems. Because some Cr compounds have caused serious health problems from industrial exposure, and because hexavalent Cr compounds are irritating and corrosive to tissues and are highly oxidative, the role of chromium in the environment requires careful consideration (Nat. Acad. Sci. 1974).

Cobalt

Cobalt salts given orally in excess causes polycythemia, with hyperplasia of the bone marrow and goiter in children. Cobalt does not produce toxic effects in humans under normal circumstances. When cobalt was added to beer to improve the stability of foam, numerous human fatalities occurred. Autopsies showed lesions and enlarged hearts. The "beer drinker's syndrome" disappeared with removal of cobalt. When cobalt is injected intravenously, large doses cause paralysis, enteritis and sometimes death. Co injected in rats causes a high incidence of cancer, namely rhabdomyo-sarcoma. Cobalt has an inhibitory effect on cell oxidative metabolism. Cobalt intake has also been linked to development of hardening of the arteries (atherosclerosis) (Friberg 1977 and Schroeder et al. 1967).

An important naturally occurring cobalt coordinaton compound is vitamin B12, the antipernicious-anemia factor. Cobalt compounds are added to livestock feeds, salt-licks and fertilizers to prevent cobalt deficiency since small quantities are essential.

Gastrointestinal absorption is about 25 percent. The major part is excreted within days in the urine but about 10 percent has a biological half life of about two years (Friberg 1977).

Copper

Accidental ingestion of large amounts of copper salts causes gastrointestinal disturbances. Inhalation of copper fumes may cause metal or fume fever. Chronic copper poisoning has not been described in normal human beings. Systemic effects, especially hemolysis, liver damage, and renal damage have been reported after ingestion of large amounts of copper salts, but recovery has usually been rapid upon removal from exposure and treatment. In industry, copper exposure is common but chronic effects have not been reported. Lung changes have been reported in vineyard workers spraying vines with copper sulfate solutions. Since other compounds may contribute, the role of copper in these cases has not been fully elucidated (Friberg 1977).

Copper absorption from food is about 50 percent and is normally regulated by homeostatic mechanisms. It is mainly stored in the liver, muscles, and excreted mostly via bile.

Lead

There are numerous toxic effects of lead of variable severity. Severe clinical lead poisoning causes an array of effects on the central nervous system, the gastrointestinal system, the hemopoietic system, and the kidneys. The thyroid gland, heart, and other organs may also be involved to varying degrees. In severe cases, profound disturbances of the central nervous system are prominent, and permanent damage to the brain may occur. Damage to the kidneys occurs and may be permanent. The life span of erthrocytes is shortened, with or without coexistent anemia. In light cases, mild anemia, headaches, and generalized muscle pains occur, generally followed by constipation and diffuse abdominal pain. Chronic exposure may cause dulling of mentation and chronic hyperkinesis. This may be a cause of aggressive behavior in ghetto and heavily exposed children in inner cities (Nat. Acad. Sci. 1972).

Lead poisoning occurs frequently in children exposed to flaking lead paint, and street contaminated dust and air from tetraethyl lead from gasoline combustion from vehicles in inner cities. Children appear to be more susceptible than adults (EPA 1976). Lead poisoning is an important occupational hazard in many industries, especially smelting, battery manufacture and printing. It also results from exposure to vehicle exhaust in garage workers and policeman, from lead glazing of pottery and from drinking improperly distilled whiskey. Urban and other populations exposed to exhaust from vehicles burning tetraethyl in gasoline are large and important targets.

Mercury

Mercury is toxic in vapor form, in the metallic state, and especially in certain mercury compounds. Mercury vapor gives rise to central nervous system symptoms such as tremor, anorexia, weight loss, irritability, anxiety, loss of self-confidence and insomnia (called micromercurialism). Advanced cases often include major changes in personality and psychoses. There may be a metallic taste, gingivitis and ptyalism (Friberg 1977).

High oral doses may cause intense local corrosive action in the gastrointestinal tract and acute renal failure. Methyl and ethylmercury poisoning include sensory distrubances in distial parts of the extremities and in the tongue and around the lips, ataxia, and concentric constriction of the visual fields (tunnel vision). Hearing loss and mental disturbances may occur, rarely proteinuria. In ethylmercury poisoning, cardiac disorders have been reported (WHO 1972).

Human hair, blood cells, and plasma mercury levels are of greatest value as indices of exposure and of levels in critical organs.

Exposure may be due to occupational exposure such as working in a mercury smelter, dental offices, chloralkali factory or other industry, or to eating Hg treated grain in bread, or fed to hogs, or eating fish and shellfish with high levels of Hg. Major outbreaks have been in Japan (Minamata disease) from industry and in Iraq, Guatemala, Pakistan and other countries from eating wheat treated with mercury.

Nickel

Nickel and its compounds in the atmosphere constitute a real health hazard. Inhaled nickel carbonyl $Ni(CO)_4$ is highly toxic and decomposes to metallic nickel which deposits on the epithelium of the lung, from where it is readily absorbed and damages the lung and brain. Nickel causes cancer of the lungs and nasal cavities, respiratory neoplasia, dermatitis, inhibition of enzyme systems, kidney damage, intestinal disorders, convulsions and asphyxia (Bowen 1966, Smith et al. 1975). Absorption through the skin has not been proven, but nickel dermatitis occurs.

Nickel refinery workers are prone to develop lung cancer and especially cancer of the nose or sinus when exposed to nickel dusts, fumes and carbonyl for many years; death rates from these causes are 2 to 25 times those expected of the general population (Sullivan 1969).

Selenium

Selenium salts are among the more toxic elemental compounds and Se has been shown to be carcinogenic and teratogenic in animals. Even at relatively low doses it is toxic and it may affect the kidneys, liver, bone marrow and central nervous system. Selenium salts are potent skin and mucous membrane irritants. Liver damage results from ingestion at 5.0 to 7.0 ppm and liver cancer at 10.0 ppm of Sè. Respiratory selenosis may result from inhalation of concentrations as low as 0.2 ppm. Se may enhance formation of dental caries.

Se has a protective effect against the toxic action of mercury and against the carcinogenic and teratogenic effects of cadmium and arsenic. Estimated dietary thresholds of Se concentration are deficiency-physiological, 0.03 ppm; excess-physiological-pathological, 0.4 ppm; excess-pathological-clinical, 3.0 ppm; excess-clinical-lethal, 20.0 ppm (Harr and Muth 1972).

Selenium can be acquired from inhalation of the dust, vapors, gases and fumes of the metal or its compounds, by ingestion, and to some extent by absorption through the skin. Se fumes cause garlic breath, gastrointestinal upset, nervousness, and damage to most organs. SeO causes broncheospasm, chills, fever, and pneumonitis (Oak Ridge Nat. Lab. 1977). "Blind staggers" and "alkali disease" of cattle, "white muscle disease" in sheep and various symptoms of subacute nature and attributed to Se (Harr and Muth 1972).

Tin

Tin in the elemental metallic inorganic form is of low toxicity to man. Inorganic derivatives, e.g., tin salts, usually have a low order of toxicity in experimental animals, regardless of the route of administration. However, small doses of tin fed to rats and mice for life decreased longevity slightly (Schroeder 1974).

Some organic alkyl tins, e.g., triethyl tin derivatives, are highly toxic, enter nerve and brain tissue and are extremely active inhibitors of metabolic processes as well. Triethyl tin is a potent uncoupler of oxidative phosphorulation (WHO 1976b).

The low toxicity of inorganic tin ingestion is largely due to low absorption, low tissue accumulation (other than in lung) and rapid turnover of the element, largely in the feces.

More definitive information is required regarding toxicity of various valence states and forms of tin, especially related to increased use and dissemination, e.g., in plastics and dentrifices. Exposure to tin fumes and dusts results in stannosis which is a benign pneumoconiosis. Acute non-fatal intoxication results from ingestion of food or fruit juices highly contaminated from tin cans and solders. Organotin has caused human deaths or acute toxic conditions (WHO 1976b).

Vanadium

In high doses, vanadium is toxic to man. The principal toxic effects have been observed in industrial workers exposed to relatively high concentrations of compounds of vanadium. Exposure to several mg/m^3 caused direct irritation of the trachea and bronchi with tightness of the chest, cough, sputum, and eye, nose and throat irritation. Chronic toxic effects are weakness, slight anemia and neurasthenia. Prolonged exposure results in emaciation, anorexia, nausea and diarrhea. Chronic exposure depresses cholesterol synthesis, oxidative phosporylation in liver mitochondria is uncoupled, and urinary excretion of 5-hydroxyindoleacetic acid occurs with transient bilirubinuria and albuminuria (Nat. Acad. Sci. 1974a).

Other symptoms include "green tongue," and scattered eczematous skin lesions, some of which appear to be allergenic. Changes have been found in cardiovascular functions, and lowering of cystine and cysteine synthesis.

Vanadium salts are poorly absorbed by the intestine and when absorbed are rapidly excreted. Small amounts are stored in bone and are mobilized slowly. Oral ingestion of vanadium is not considered to be a hazard. There is some evidence that vanadium is an essential element for laboratory animals, and may be involved as a type of oxygen carrier in some ascidians or tunicates.

TOXIC TRACE METALS IN THE ENVIRONMENT

Data on abundance, production, uses, environmental emissions and dispersion, sources and pathways to biological organisms are of importance in defining the extent of pollution and the priorities for each trace metal. This information is important in selecting appropriate biological monitoring organisms, the type of monitoring required, and the number and geographic distribution of sites required.

The abundance of the selected trace metals in the earth's crust, in dry soil, in the ocean, and in freshwater are shown in Table 2. This presents background information relative to baselines and backgrounds in non-polluted areas. Toxic trace metal abundance in the earth's crust for the 14 selected elements is 0.2 to 135.0 ppm and 0.2 to 100.0 in dry soil. Their abundance in the ocean is from 0.0000006 to 0.003 ppm (with 4.6 ppm for B), and in freshwater from 0.00004 to 0.13 ppm. This gives an estimate of the relative abundance of the trace metals in comparison with iron in the earth's crust (56,300 ppm), and calcium (41,500 ppm), or sodium in seawater (10,500 ppm), and magnesium (1,350 ppm).

To provide an indication of the amount of pollution or potential pollution for each trace element, the annual world production, annual consumption (United States) and an estimate of the annual air pollution emissions in the

TABLE 2. ABUNDANCE OF TRACE METALS IN THE ENVIRONMENT* (in ppm)

	Igneous Rocks, Earth's Crust	Soil (dry)	Ocean	Freshwater
Antimony	0.2	2.0-10.0	0.00033	
Arsenic	1.8	6.0	0.003	0.0004
Beryllium	2.8	6.0	0.0000006	0.001
Boron	10.0	10.0	4.6	0.013
Cadmium	0.2	0.06	0.00011	0.08
Chromium	100.0	100.0	0.00005	0.00018
Cobalt	25.0	8.0	0.00027	0.0009
Copper	55.0	20.0	0.003	0.01
Lead	12.5	10.0	0.00003	0.005
Mercury	0.08	0.03	0.0001	0.00008
Nickel	75.0	40.0	0.0054	0.01
Selenium	0.05	0.2	0.00009	0.02
Tin	2.0	10.0	0.003	0.00004
Vanadium	135.0	100.0	0.002	0.001

* Data from Bowen (1966)

United States are presented in Table 3. For each trace metal, the abundances, mining and production data, major uses, sources and environmental contamination data are presented. The major sources and pathways to biological organisms of each toxic trace metal have been listed in outline form. This has been derived from data on sources, pollutant emissions, various uses of the trace metals, studies of use of biological organisms in measuring environmental gradients of the selected trace metals, and from published studies on the exposure, uptake and ingestion, and external contamination. While the sources and pathways listed are fairly extensive, there are undoubtedly others which are of importance and could be included.

TABLE 3. TOXIC METAL PRODUCTION, USE, AND AIR POLLUTION (1,000 metric tons)

	World Production 1976[a)]	U.S. Consumption 1976[a)]	Man-Caused Air Pollution in U.S. 1 yr.[b)]
Antimony	75.065	34.581	0.25
Arsenic	39.28	4.196	9.76
Beryllium	10.0[c)]	0.519	0.45
Boron	2,263.68	110.23	10.5
Cadmium	18.594	5.886	0.4
Chromium	4,203.9	284.44	16.46
Cobalt	28.228	8.287	0.75
Copper	8,083.09	2,206.60	200.0
Lead	4,625.79	1,466.47	234.5
Mercury	8.429	2.241	20.0
Nickel	872.342	160.35	4.885
Selenium	1.364	0.486	0.50
Tin	225.24	61.934	30.0
Vanadium	25.537	4.65	20.0

a) U.S. Bur. Mines (1978)

b) Data from Bertine and Goldberg (1971) and Jenkins (1976)

c) Friberg (1977)

To clearly define the problems, needs and priorities for biological monitoring for each pollutant, it is necessary to describe the amount and dispersion of each trace metal. A search was made for accurate and recent mass-balance studies for each pollutant but because no recent concise reports were available, emission and dispersion data were obtained from scattered sources.

Antimony

Abundance and Use

Elemental antimony is usually a crystalline, silver-white solid metalloid, and is one of the rarer trace elements. Its abundance is from 0.22 to 1.0 ppm in the earth's crust and about 0.11 to 0.45 ppm in the ocean. It is found in many minerals, but the main commercial ore is stibnite (Sb_2S_3) which is mined in a number of countries including South Africa, China and Bolivia.

The world production in 1971 was 63,000 tons and in 1976 was 75,065 metric tons. The United States in 1976 used 15,095 tons of new antimony and 19,486 tons of antimony recycled from scrap. By year 2000 it is estimated that the United States will use 81,000 tons (U.S. Bur. Mines 1978).

Antimony ore is obtained by both smelting and chemical extraction. It also occurs in coal and oil. Antimony usage in 1968 in the United States was for production of storage batteries (47 percent), ammunitions, wire and castings (19 percent), fire retardants (9 percent), chemical pigments (7 percent) and other (9 percent) (WHO 1976a).

Sources and Environmental Contamination

Antimony pollution occurs from wastes from foundries, battery manufacture, recycling facilities, rubber and chemical plants and in industrial and domestic sewage and sludges.

Antimony is highly toxic but few quantitative data are available on exposures, sources and transport. In the Boston area, Sb had an atmospheric enrichment factor of 2,700 relative to the earth's crust. In San Francisco the enrichment factor was 41,000 and in northwest Indiana 1,230. Municipal incineration and combustion of coal and residual oil, especially in fly ash and leachate from various containers, are also sources of antimony pollution. (WHO 1976a).

It is difficult to visualize the geographic distribution of Sb except that it is widespread in small quantities with highest levels in industrial areas from combustion of fuels and refuse. Little is known of transport from natural sources.

Sources and Pathways to Biological Organisms

Antimony is relatively rare, but is fairly widely distributed. It occurs naturally in some soils, seawater, and some freshwaters, but the highest concentrations occur as the result of man's activities. An important method of contamination is airborne, and certain urban areas have relatively high levels of Sb. The sources are not completely known but incineration of coal, oil, refuse, smelting and industry are usually blamed.

The major pathways of Sb to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. From soil contaminated by fallout of air pollution.
        b. From natural Sb content of soil.
    2. Plant contamination from air.
        a. Incineration of coal, oil, refuse.
        b. From industry and smelters.

b. Animals
    1. Terrestrial
        a. From eating plants containing Sb.
        b. From drinking Sb in water and breathing it in air.
    2. Aquatic
        a. From naturally occurring Sb in water.
        b. From man-caused pollution wastes from industry and domestic sources.
        c. From ingestion of algae and other organisms.

Arsenic

Abundance and Use

Arsenic ranks twentieth in abundance among the elements with 1.5 to 2.0 ppm in the earth's crust. It is widespread and commonly found in many minerals, especially in sulfide deposits. The content of freshwater for drinking is usually 0.01 to 0.1 ppm and the mean value of river water is 0.004 ppm. Seawater ordinarily contains from 0.006 to 0.03 ppm of As.

Arsenic is present in appreciable amounts in many lead, zinc and copper ores and is obtained as a byproduct in smelting. While emission of arsenic presents a problem in smelters treating these ores, the only United States plant recovering arsenic is at Tacoma, Washington.

The world production of arsenic in 1976 was 39,280 metric tons (excluding U.S. production). The United States consumption of As in 1973 was 23,808 metric tons of which about 17,500 tons was imported and consumption in 1976 was 4,196 metric tons (U.S. Bur. Mines 1978). About 97 percent of the arsenic produced is in the form of white arsenic trioxide.

In the United States in 1973, about 81 percent of the arsenic (trioxide) was used for arsenical pesticides for agriculture including lead arsenate, calcium arsenate, sodium arsenite and organic arsenicals. These compounds are used in insecticides, herbicides, fungicides, algicides, sheep dips, wood preservatives and dye stuffs and for eradication of tapeworm.

Sources and Environmental Contamination

In the United States in 1974 there was a total movement of 108,000 metric tons of arsenic. The dissipation to the land was 63,030 short tons of which steel slag was 39,690 tons, pesticides 11,565 tons, copper leach liquor and other 11,775 tons. The airborne emission was 9,757 short tons of which losses from copper smelting was 5,292 tons, pesticides 2,536 tons, coal 717 tons and petroleum and other 1,212 tons. The waterborne effluent was 165 metric tons of which phosphate detergents was 121 tons (Nat. Acad. Sci. 1977, Oak Ridge Nat. Lab. 1977).

Sources and Pathways to Biological Organisms

Arsenic appears everywhere in nearly every living tissue and is constantly being oxidized, reduced or otherwise metabolized. About half of the mobile arsenic comes from the use of pesticides and much comes from smelting operations. Arsenic from man-made sources eventually reaches the soil. Processed arsenic is applied by way of pesticides and through natural contamination of fertilizer materials. Arsenic that is gaseous or adsorbed onto particulate matter is removed from the atmosphere through fallout or in rain. It is deposited on the vegetation, on soil, or in water. In the soil environment, insoluble or slightly soluble compounds are constantly being resolubilized and arsenic presented for plant uptake or for reduction by organisms and chemical processes. Man has modified the arsenic cycle only by causing localized high concentrations (Nat. Acad. Sci. 1977).

The major sources and pathways of As to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring As in the soil.
        b. From pesticides, herbicides, insecticides, fungicides on soil.
        c. From fertilizers, sewage, sludge, fallout on soil from smelters, industry and waste and fuel incineration.
    2. Plant contamination from the air.
        a. From pesticides, insecticides and herbicides on the plants.
        b. Fallout on plants from smelters, fuel and waste incineration smelters.

b. Animals
    1. Terrestrial
        a. From eating plants containing and/or contaminated with As.
        b. From drinking water containing As.
        c. For predatory and scavenger animals, from eating animals containing As, and poison baits.
        d. For domestic animals, from feed additives, and treatment for parasites and insects.

2. Aquatic
   a. From runoff and aerial deposition from smelters, mines, tailings leachates, runoff, fuel consumption, and incineration, sewage and industrial wastes.
   b. From eating plants and animals containing As.
   c. From pesticides, insecticides and algicides and herbicides.
   d. From As naturally occurring in hot springs, artesian wells and geothermal electric projects.

Beryllium

Abundance and Use

Beryllium is fairly rare and the earth's crust contains about 2.8 ppm. It is found in beryl ore (to 5 percent Be) and bertrandite in commercial quantities. There is from 0.0006 to 0.001 ppb Be in seawater and from 0.1 to 1.0 ppm in river water (Oak Ridge Nat. Lab. 1978).

The world production of Be (Beryl?) was about 10,000 metric tons per year (Friberg 1977). World production was 4,203.9 metric tons reported in 1976. The United States production is from 45 to 68 tons per year, and the consumption in 1976 was 4,720 metric tons of beryl with 11 percent Be or 519.0 metric tons of Be (U.S. Bur. Mines 1978). Estimated U.S. demand for year 2000 is 1,500 metric tons.

Beryllium is used as the free metal in about 20 percent of world uses. It is used for missile and nuclear reactor components, rocket nozzles, aircraft brakes, electrical relays, space optics, space vehicle reentry cones, X-ray windows and inertial guidance parts. Be alloys, which compose 72 percent of the use, are 96 percent Cu and 4 percent Be. These are used for springs, welding components, bearing sleeves and underseas cable housing. BeNi alloy is used in diamond drill bits, watch balance wheels, and aircraft and spacecraft parts. About 8 percent of Be is used as oxide in ceramic formulations for resistor cores, integrated circuit chips and radio and laser tubes.

Sources and Environmental Contamination

In 1968 in the United States, about 133 metric tons of Be was emitted to the atmosphere from coal combustion, 7.3 tons from oil combustion, 14.5 tons from the ceramic industry, and 3.6 tons from cast iron production. A total of 148 metric tons was emitted to the U.S. atmosphere in 1968 (EPA 1971). According to Sax (1974) (cited in Oak Ridge Nat. Lab. 1977) 410 metric tons of Be were mobilized annually into the atmosphere from coal combustion based on 1967 production figures.

The geographic distribution of Be is related to coal combustion and specific areas where Be is manufactured into products or when it is used. The distribution then is somewhat general from coal combustion and highly localized with regard to human use and manufacture of Be materials.

Sources and Pathways to Biological Organisms

Be is relatively rare and is naturally abundant only in concentrations in beryl in pegmatites or in bertrandite ore areas. Most dissemination of Be is due to the activities of man. The major amount is disseminated into air from combustion of coal and oil. It occurs in coal (1.0 to 1,000 ppm) and in fly ash (12.0 to 62.0 ppm). Be concentrations in air have been found around beryllium processing plants with decrease with increased distance from the stack. Beryllium has also been found in some metropolitan areas, highest in Philadelphia and Detroit (cited in Oak Ridge Nat. Lab. 1978).

There are few data on Be in biological organisms or foods.

The major sources and pathways of Be to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring Be in soil.
        b. Be deposited on ground as fallout.
    2. Plant contamination from air.
        a. From fallout from coal and oil combustion.
        b. Fallout around Be processing facilities.

b. Animals
    1. Terrestrial
        a. From eating plants containing Be.
        b. From breathing air or drinking water containing Be.
        c. From eating other animals containing Be.
    2. Aquatic
        a. From naturally occurring Be.
        b. From eating plants and animals containing Be.

Boron

Abundance and Use

Boron is not uncommon and is about 3 ppm of the earth's crust. It is concentrated in deposits of hydrated borate minerals that are easily worked. There is about 10 to 100 ppm of boron in igneous and sedimentary rocks. There is 4.6 ppm of B in seawater and 0.004 to 1.76 ppm in freshwater.

The world production of boron in 1976 was over 2,263,680 metric tons. The United States consumption was 110,000 tons and it is the major producer (1,246,000 short tons/year) (U.S. Bur. Mines 1978).

Borates are used in manufacture of borosilicate glasses, ceramic glazes, vitreous enamels, detergents and water-softening agents, flame-proofing materials, preservatives, fluxes, insulation fiberglass and textile fiberglass. About 8,000 tons of boron are used each year for algicides, water treatment, fertilizer, herbicides, and insecticides. Boron is used by the pulp and paper industry for bleaching ground wood. It is also used as a hardener for other metals and as a neutron absorber in nuclear installations.

Sources and Environmental Contamination

Coal contains about 75 ppm and 10,500 tons of B are mobilized into the atmosphere per year (Sax 1974). Fly ash from fossil fuel also contains considerable quantities of boron. Fairly large quantities of B are put into water.

Boron is not of much danger to man due to its low toxicity, so that the sources and dispersion are not of great importance.

Sources and Pathways to Biological Organisms

Boron is widely available to organisms from natural sources; however, it is naturally concentrated in certain localities. It is dispersed into the environment by man and combustion of coal is a major source of atmospheric pollution and fallout.

The major sources and pathways of B to biological organisms are:

a. Plants
  1. Uptake by roots from soil.
    a. Naturally occurring B in soil and irrigation water.
    b. Fallout on soil from combustion of coal.
    c. From fertilizers, herbicides and insecticides.
  2. Plant contamination from the air.
    a. Fallout from combustion of coal.
    b. From herbicides and insecticides.

b. Animals
  1. Terrestrial
    a. From eating plants or animals containing and/or contaminated with B.
    b. From breathing air or drinking water containing B.
  2. Aquatic
    a. From naturally occurring B.
    b. From eating plants or animals containing B.
    c. From runoff of pesticides, fertilizers, herbicides and from pulp paper industry.

Cadmium

Abundance and Use

Cadmium is a relatively rare element in the earth's crust and ranks between mercury and silver in abundance, 0.1 to 0.5 ppm, and 0.02 ppb in the oceans. It is obtained as a byproduct in zinc smelting and refining.

The world production of cadmium in 1976 was 18,594 metric tons. World demand in the year 2000 is estimated to be between 25,000 and 49,500 tons. Cadmium is not concentrated in minerals, but is produced in conjunction with zinc refining. United States consumption in 1976 was 5,886 metric tons. Of the total use in 1975 about 55 percent was used in electroplating, 20 percent in plastic stabilization, 12 percent in pigments, 5 percent in batteries, and 8 percent miscellaneous (U.S. Bur. Mines 1978).

Sources and Environmental Contamination

Of about 2,000 metric tons of Cd emitted to the environment in the United States in 1974, about 50 percent was from fuel combustion, 30 percent from industrial uses, remelting Cd scrap and incineration of rubber and plastics, and 20 percent from zinc mining and smelting. Cadmium is a contaminant in phosphate fertilizer and from 100 to 200 tons of Cd were estimated to be put on soil in 1975. Cadmium in sewage sludge was estimated at 300 tons with 60 percent applied to land, 10 percent dumped at sea and 30 percent incinerated. Recent changes in cadmium production and emission patterns in the United States have resulted in a total emission estimate of 1,800 tons for 1974-1975 and 2,100 tons for 1980. The airborne emissions are about 300 tons, waterborne effluents 25 tons for 1974-1975, and 15 tons 1980, and land destined wastes 1,500 tons 1974-1975, and 1,800 tons for 1980 (Sargent and Metz 1975).

Sources and Pathways to Biological Organisms

Cadmium is not highly concentrated naturally in certain minerals or sites so that there are no known plant or animal populations with long evolutionary experience or adaptations to the element. Relatively low levels of naturally occurring Cd are found in soil and water. Higher levels are caused by man from fairly well known sources and pathways.

The major sources and pathways of Cd to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring Cd in soil.
        b. Cd in super phosphate or sewage sludge fertilizers.
        c. Soil contamination from mine tailings, electroplating pollution, industry, and fallout from air pollution.
        d. From fungicides, herbicides and pesticides on soil.
    2. Plant contamination from the air.
        a. Around zinc or other smelters and refineries.
        b. Incineration of coal and oil, plastics and rubber tires.
        c. From fungicides, herbicides, and pesticides on plants.

b. Animals
    1. Terrestrial
        a. From eating plants containing and/or contaminated with Cd.
        b. From drinking water containing Cd.
        c. From breathing air containing Cd especially around smelters or in urban areas.
        d. For predatory and scavenger animals, from eating other animals containing Cd.

e. For domestic animals, from drinking water contaminated from zinc galvanized pipe or polyethylene pipe.

2. Aquatic
   a. From runoff and aerial deposition from smelters, mines, tailings leachate and runoff, incinerators, sewage and industrial and electroplating and other wastes from outfalls, dumps and runoff.
   b. From eating plants and animals containing Cd.
   c. For filter feeders, from food, metal uptake from solution, and from ingestion of organic and inorganic particulate matter containing Cd.

For most organisms, cadmium is absorbed and accumulated or bioconcentrated and stored in the organisms. However, for plant surfaces and especially for spanish moss, lichens and moss, and for animal hair and feathers, external contamination must be considered in making analyses. The external contamination data are of value in determining source, pathway, and total environmental contamination.

The source of cadmium pollution appears to influence the ability of certain marine fauna to accumulate it. According to Preston (1973), oysters apparently accumulate cadmium from an industrial source to a greater extent than cadmium of geochemical derivation.

Chromium

Abundance and Use

Chromium is fairly abundant and averages about 125 ppm in the earth's crust, being more abundant than copper, zinc, lead, nickel or cadmium. It is widely distributed and is concentrated especially in South Africa, the USSR, Turkey, Finland, the Philippine Islands, Brazil, the United States and other areas. There is about 0.04 ppb Cr in seawater and freshwater contains 0.1 to 80.0 ppb. It is usually mined as chromite.

The world production of chromium in 1968 was 1,664,000 tons and in 1976 was 4,203,900 metric tons (9,342,121 tons of chromite ore). In 1976, the United States consumption was 284,440 metric tons which represents 993,068 tons of chromite ore. In the United States 59.3 percent was used by the metallurgical industry, 20.1 percent by the refractory industry, and 20.1 percent by the chemical industry (U.S. Bur. Mines 1978). Chromium is used in a large number of industries with major use in metallurgy, and in chemical compounds used for paints and dyes, tanning leather, metal plating and many other uses.

Sources and Environmental Contamination

In the United States in 1970, emissions of chromium, after controls, was 16,463 tons of which 68.2 percent was from ferrochromium refining and 8.6 percent from coal combustion. Phosphate fertilizer contains 175 to 344 ppm of Cr. Electroplating wastes are a major contributor to sewage effluent as are the tanning industry, chromite pigments, and urban housing areas. Chromium is used in cooling towers as a corrosion inhibitor (Oak Ridge Nat. Lab. 1976, 1977).

Chromium is abundant but is not highly toxic. The main concern for chromium toxicity is occupational exposures. Fairly large quantities of chromium are emitted into the general environment from the refining and metals industries, coal combustion and natural sources, but presently there is not much concern as a hazard to man.

Sources and Pathways to Biological Organisms

Chromium is relatively common and widely distributed so that plants and animals have a long evolutionary experience and adaptation to it. It occurs in abundance naturally in serpentine and Cr ore areas in many parts of the world. Most Cr in soils is apparently insoluble and therefore, not readily available for plant uptake. Man disseminates it in large quantities and many species of plants and animals are exposed.

The major sources and pathways of Cr to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring Cr in soil, especially in serpentine and Cr ore areas.
        b. Soil contamination from fallout from the metallurgical industry and incineration of coal, oil and refuse.
        c. From electroplating, leachate, fertilizers and sewage sludge and dumps.
    2. Plant contamination from the air.
        a. From emission from foundries, and other industries.
        b. From combustion of coal, oil and refuse.

b. Animals
    1. Terrestrial
        a. From eating plants containing and/or contaminated with Cr.
        b. From breathing air and drinking water containing Cr.
        c. For predatory and scavenger animals from eating other animals containing Cr.
    2. Aquatic
        a. From naturally occurring Cr (hexavalent Cr is the major stable form in seawater).
        b. From runoff and aerial deposition from foundries, smelters, incinerators, and leachate from sewage and industry, especially electroplating and leather industry.
        c. From eating plants and animals containing Cr.

Cobalt

Abundance and Use

Cobalt is widely distributed in nature making up about 25.0 ppm of the igneous rocks of the earth's crust. There is 0.5 ppb of Co in the ocean and 0.1 to 5.0 ppb in freshwater.

Cobalt is found in many ores of iron, nickel, copper, silver, manganese and zinc. It is produced in Canada, Zambia, Morocco and the USSR but deposits occur in other countries.

The world production of cobalt was 28,228 metric tons in 1976. The United States imported and consumed 8,287 tons in 1976. About 80 percent of the world output is used in the metallic state, particularly in alloys for high temperature metals, magnets, cutting tools, and electrical resistance alloys. It is also used in the glass and ceramic industry and for catalysts and pigments (900 tons) (U.S. Bur. Mines 1978).

Major uses in 1976 in the United States for Co were 18 percent for aircraft, 28 percent for electrical magnets, 16 percent for cutting tools, 15 percent for paints, mainly driers, 12 percent for ceramics and 9 percent for chemicals. Pigment use increased 60 percent in 1976 (U.S. Bur. Mines 1978).

Sources and Environmental Contamination

Cobalt intake by man is about 5.0 to 40.0 µg per day from food. Drinking water contains usually between 0.1 to 50.0 µg/l. Co in ambient air was found (70.3 ng/m^3) in only 90 of 750 air samples from 28 stations in the United States (cited in Friberg 1977). Pneumoconiosis occurs only from occupational exposure to contaminated atmosphere.

Coal contains about 5.0 ppm Co and based on 1967 production figures in the United States, 700 metric tons of Co was mobilized annually into the atmosphere from coal combustion and 30 metric tons from oil combustion (Oak Ridge Nat. Lab. 1977).

Sources and Pathways to Biological Organisms

Cobalt is disseminated into the environment by man mainly from combustion of coal and oil, with a smaller amount from smelters, cobalt processing plants, some cobalt products, and sewage and industrial sewage.

The major sources and pathways of Co to biological organisms are:

a. Plants
  1. Uptake by roots from soil.
    a. Naturally occurring Co in the soil.
    b. Fallout from combustion of coal and oil and from smelters.

2. Plant contamination from the air.
    a. Fallout from combustion of coal and oil.
    b. Around smelters and Co processing facilities.

b. Animals
   1. Terrestrial
      a. From eating plants and animals containing Co.
      b. From drinking water and breathing air containing Co.
   2. Aquatic
      a. From eating plants or animals containing Co.
      b. From sewage and industrial wastes.
      c. From naturally occurring Co in the water.

Copper

Abundance and Use

Copper is a common metal and its abundance is 20 ppm in dry soil and 55 ppm in igneous rock. Its abundance in seawater is 0.003 ppm, and from 0.0006 to 0.4, median 0.01 ppm, in river water (Oak Ridge Nat. Lab. 1977).

The main copper ores are cuprite, malachite, azurite, chalcopyrite and bornite, with sulfide ores about 75 percent of the production.

The world production of copper in 1976 was 8,083,090 metric tons. The consumption in the United States in 1976 was 2,206,600 metric tons or an increase of 30 percent from 1975. Wire mills accounted for 68 percent of refined copper consumption, brass mills 29 percent and other 3 percent. Sulfuric acid byproduct at 14 smelters increased to 2,245,573 metric tons in 1976 (U.S. Bur. Mines 1978).

The primary use of copper, accounting for about one half of the production, is for electrical equipment. Copper is a component of many alloys in which it is combined with silver, cadmium, tin and zinc. It is also used in plumbing and heating. Copper salts are used in insecticides, algicides, and other pesticides.

Sources and Environmental Contamination

The copper mobilized into the atmosphere from combustion of coal is 2,100 metric tons per year. Weathering mobilization contributes about 250,000 tons per year in river flow (Sax 1974).

Copper is also introduced into the environment from copper mining and smelters, pesticide uses, sewage outfalls and sludge. The total man-caused air pollution has been estimated at about 200,000 tons per year.

Sources and Pathways to Biological Organisms

Copper is relatively abundant and is mined and used in great quantities by man. With about 200,000 tons emitted into the air and 250,000 tons into rivers each year, there is high Cu mobilization and transport which causes relatively high exposure to biological organisms.

Since Cu is of relatively low toxicity to mammals there is not much concern for Cu pollution in comparison with Pb and Cd.

The major sources and pathways of Cu to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring Cu in soil and ground water.
        b. From fallout on soil of Cu emitted from smelters and combustion of coal and refuse.
        c. From sewage sludge and other fertilizers.
        d. From soil contamination from use of biocides and pesticides.
    2. Plant contamination from the air.
        a. From fallout from Cu emitted from smelters, steelworks, mining operations and combustion of coal and refuse.
        b. From application of pesticides and biocides.

b. Animals
    1. Terrestrial
        a. From breathing air containing Cu from smelters, mining, steelworks, combustion of coal and refuse.
        b. From eating plants containing or contaminated with Cu.
        c. For predatory and scavenger animals from eating other animals containing Cu.
        d. From drinking water containing Cu.
    2. Aquatic
        a. Naturally occurring Cu in water.
        b. Water pollution from runoff and fallout from air emissions.
        c. From sewage and industrial waste outfalls, dumps, and deposit areas, and effluent from thermoelectric plants.
        d. From tailings, leachate, and mine and smelter effluent.
        e. From eating plants and animals containing Cu.
        f. From filter feeding of inorganic sediment containing Cu.
        g. From biocides, especially algicides.

Bioaccumulation is quite high in most groups of animals and in both higher and lower plants. Use of copper sulfate and other copper pesticides and biocides has been reduced greatly so that levels of Cu from these sources has been decreased.

Lead

Abundance and Use

Lead is an abundant and widely dispersed toxic metal element with an average concentration of 12.5 ppm in the earth's crust. It is mined in lead ore deposits, especially galena (PbS), and occurs in many other minerals. Its abundance in seawater is 0.05 ppb and in fresh water is 1.0 to 10.0 ppb and 5.0 ppb (WHO 1977).

World production of lead in 1976 was 4,625,790 metric tons. United States consumption in 1976 was 1,466,470 metric tons, of which 55 percent was for battery manufacture, 16 percent for gasoline antiknock compounds, 7 percent for pigments, 5 percent for ammunition and 17 percent for other uses (U.S. Bur. Mines 1978).

Sources and Environmental Contamination

World use of lead for antiknock additives was 380,000 tons of Pb in 1973 (International Lead and Zinc Group 1976). Lead for gasoline antiknock additives in the United States in 1976 was 235,972 metric tons, an increase of 15 percent above the 1975 level of 205,311 metric tons (U.S. Bur. Mines 1978). This constitutes a grave and increasing danger to human beings despite the partial use of lead free gasoline. About 210,000 tons of Pb was emitted to the air from this source in 1975, plus 1,900 tons from manufacturing lead additives (WHO 1977). About 70 percent of the lead in gasoline is emitted to the air. Much of the other 30 percent remains in used engine oil which is about 1 percent lead of 24,000 tons of lead, most of which is burned instead of being re-refined (Schroeder 1974) so that most of the lead added to gasoline will end up in the air, with over 200,000 metric tons in the United States in 1976.

Secondary lead accounts for about 50 percent of the consumption in the United States and about 35 percent in the total world supply. Secondary smelters add pollution to the air in addition to smelters for primary production, which in the United States caused about 19,000 tons of Pb emission. This air pollution was caused by mining, smelting, refining, and manufacture of Pb products. There was additional air pollution 3,500 tons of Pb from burning coal (Sax 1974). Incineration of solid wastes contributed 10,010 metric tons to the atmosphere in 1968. Domestic use of lead arsenate was 2,285 metric tons in 1972 (EPA 1976).

Weathering mobilization adds about 110,000 tons to river flow per year in addition to the amount added directly or from fallout into water.

Sources and Pathways to Biological Organisms

Lead is relatively abundant naturally, and man has mobilized additional lead in increasingly larger quantities each year into the environment.

The emission of over 200,000 metric tons of Pb into the air from tetraethyl lead in gasoline in the United States in 1976 was the major source of lead contaminating plants and animals. All other sources from smelters, combustion of coal, oil and refuse, and battery manufacture was about 25,000 metric tons.

Many types of organism absorb high levels of lead and accumulate it, resulting in very high concentrations. Lead has become ubiquitous, and increasing levels have been measured in glaciers in the arctic and antarctic. It is therefore presently difficult to determine baseline data on natural levels in uncontaminated areas.

The major sources and pathways of lead to biological organisms are:

a. Plants
   1. Uptake by roots from soil.
      a. Naturally occurring Pb in soil and ground water.
      b. From fallout on soil from Pb in gasoline additives, smelters, coal, oil and refuse combustion, and other sources.
      c. From sewage sludge fertilizer.
      d. From residue from pesticides in soil.
      e. Contaminated runoff waters from used oil, fallout and other sources of water contamination.
   2. Plant contamination from the air.
      a. From fallout from Pb in gasoline additives.
      b. From fallout from smelters and combustion of coal, oil and waste.
      c. From application of Pb containing pesticides.

b. Animals
   1. Terrestrial
      a. From breathing air containing Pb from lead in gasoline, around smelters and from coal and refuse combustion.
      b. From eating plants containing or contaminated with Pb.
      c. For predatory and scavenger animals from eating other animals containing Pb.
      d. From drinking water contaminated with Pb.
      e. From licking contaminated fur, e.g., cats, or preening feathers.
   2. Aquatic
      a. Naturally occurring Pb in the water
      b. Pollution from runoff and fallout.
      c. From sewage and industrial waste outfalls.
      d. From tailings leachate and mine and smelter wastes.
      e. From eating plants and animals containing Pb.
      f. From eating lead shot.

Many plants and animals accumulate and store Pb. Plants are bioaccumulators and may show very high levels, especially from deposition of lead on the leaves in highly polluted areas such as around smelters and near highways or in cities with heavy traffic.

Mercury

Abundance and Use

Mercury is ubiquitous and widespread, and its abundance in the earth's crust is about 0.05 ppm. It also occurs in concentrated mercuriferous belts mostly as sulfides. The concentration in seawater is about 0.1 ppb, groundwater 0.05 ppb, and drinking water usually below 0.1 ppb.

World production of mercury in 1976 was 8,429 metric tons. The United States consumption was 2,241 metric tons, which was a 28 percent increase from the 1975 level. Of the major uses, electrical apparatus rose 62 percent, mildew-proofing paint rose 13 percent, and use in production of chlorine and caustic soda rose 5 percent (U.S. Bur. Mines 1978).

Sources and Environmental Contamination

There is perhaps 137 million metric tons of Hg in the ocean. In the history of man's use of Hg, less than 300,000 tons has been mined, and even if all of it ultimately went into the ocean it would have little effect on Hg levels in the ocean. High levels of Hg in tuna fish and swordfish are not due to pollution by man.

Natural degassing of the earth's crust is estimated at 25,000 to 155,000 tons per year and mercury fallout from rainfall at 30,000 tons. Natural runoff from rivers to the ocean is estimated at 5,000 tons/year. Although 75 percent of the mercury mined by man is theoretically reusable, some authorities think most or all of it will end up in the ocean.

It is estimated that 5,000 tons of Hg is emitted to the atmosphere by burning fossil fuels, 2,000 tons from smelting ores, 5,000 tons from cement and phosphate and heating processes. The estimated release of Hg to the atmosphere in 1975 (Korringa and Hagel 1974) was 20,000 tons and 30,000 tons from natural sources (or up to 150,000 tons/year). Sewage sludge could release 1,000 tons of Hg.

Annual emission of mercury to the environment in the United States according to Battelle (1977) was 1,525 metric tons in 1973 of which 4 percent was from mining and smelting Hg and other ores, 21 percent from manufacturing, 65 percent from use and disposal of Hg products, and 10 percent from coal and other fuels. The major portion, 63 percent of these emissions, was land-destined waste, air emissions were 31 percent, and water-borne effluents 6 percent. The release of Hg from natural sources to air and water are double the man-related losses to these media (Battelle 1977). These recent estimates are much lower than earlier estimates. There has also been a real decrease in pollution recently due to the publicity and Hg scares and to regulatory efforts of government agencies.

Levels of Hg in aquatic biota, both freshwater and marine, are highest on the industrialized Atlantic coast. In the Pacific Northwest United States, regionally high values occur due to both mining activity and leaching of soils naturally high in Hg. Other high levels of Hg occur scattered throughout the United States, associated with point sources of Hg emissions such as chlor-alkali and sewage treatment plants, pulp paper mills, or non-point source runoff from agricultural or other use of mercurial fungicides.

Sources and Pathways to Biological Organisms

Mercury occurs throughout the world from both natural and man-made sources. It has many uses and has been put into the environment by man in many ways. It is readily absorbed and retained in many large or long-lived organisms. The major sources and pathways of mercury to plants and animals are:

a. Plants
  1. Uptake by roots from soil.
    a. Naturally occurring Hg in the soil and groundwater.
    b. Hg in fertilizers and sewage sludge.
    c. From fallout in precipitation to the ground.
    d. From use of Hg pesticides especially seed treatment.
    e. Soil contamination from leachate and effluent especially from the chloralkali industry.
  2. Plant contamination from the air.
    a. From naturally occurring Hg in the air.
    b. From air polluted by activities of man, smelting, burning coal, etc.
    c. By fallout in precipitation on plants.
    d. By application of pesticides and biocides.

b. Animals
  1. Terrestrial
    a. From eating plants containing Hg.
    b. From eating animals containing Hg.
    c. From breathing air containing Hg.
    d. From drinking water containing Hg.
    e. From eating Hg treated seeds.
  2. Aquatic
    a. From naturally occurring Hg in water.
    b. From runoff and leachate from chloralkali and other industries, mines and smelters.
    c. From fallout in precipitation of Hg in the atmosphere.
    d. For filter feeders from ingestion of organic and inorganic particulate matter containing Hg.
    e. From eating plants and algae containing Hg.
    f. From eating animals containing Hg.

Nickel

Abundance and Use

Nickel abundance is about 75.0 ppm of the earth's crust. It is ubiquitous in nature and occurs in air, water, soil and in most biological materials. There is about 2.0 ppb of Ni in the ocean. It is mined in Riddle, Oregon, in the Untied States, and a large smelter is located in Sudburry, Canada.

The world production of nickel in 1976 was 872,342 metric tons. The United States in 1976 imported 185,176 metric tons of Ni and total consumption was 160,350 tons. About 30 percent was used in stainless steel, 20 percent in other nickel and nickel alloys, 18 percent in electroplating, 12 percent in alloy steel and 6 percent in superalloys (U.S. Bur. Mines 1978).

Nickel is used in the production of nickel and nickel alloys, monel metal, nickel silver, cupronickel, and in electroplating and for batteries, catalysts, ceramics and dying.

Sources and Environmental Contamination

Nickel emission to the air from the metallurgical industries in 1968 in the United States was about 260 tons, emission from fuel oil combustion was 4,859 tons, from coal combustion 90 tons, and from other 35 tons, or a total of 5,244 tons of nickel emission. The wastes from nickel plating (54.4 metric tons of Ni salts/day) and phosphate rock mining was 35 tons to soil and water. Additional Ni is put into the environment from sewage and sludge (Versar 1975).

It is not known whether airborne nickel contains carbonyl, nor whether relatively small exposures of the population at large are injurious (Schroeder 1974). Poisonous nickel carbonyl is formed from a reaction between nickel and hot carbon monoxide in incinerators where nickel is found in sewage sludge or solid waste (Versar 1975) and also in cigarette smoke.

Sources and Pathways to Biological Organisms

Since nickel is fairly abundant and widely distributed it is commonly found in most biological organisms. It occurs naturally in concentrated quantities in serpentine areas and in areas with Ni ores. Ni is also concentrated in specific areas by the activities of man and various biological organisms have been used for measuring environmental gradients of Ni.

The major sources and pathways of Ni to biological organisms are:

a. Plants
   1. Uptake from soil.
      a. Naturally occurring Ni, especially in serpentine and Ni ore areas.
      b. Soil contaminated from fallout from smelters, industry, and incineration of fuels.
      c. From sewage and fertilizer.
   2. Plant contaminaton from the air.
      a. Around Ni smelters and refineries.
      b. From incineration of coal, oil and refuse.

b. Animals
   1. Terrestrial
      a. From eating plants containing Ni.
      b. From breathing air around smelters or urban industrial areas.

    c. From drinking water containing Ni.
    d. For predatory and scavenger animals from eating other animals containing Ni.
2. Aquatic
    a. From naturally occurring Ni.
    b. From runoff and aerial depositon of Ni pollution in water.
    c. From eating plants and animals containing Ni.
    d. From sewage outfalls and ocean dumps.

Selenium

Abundance and Use

Selenium is widely but unevenly distributed on earth. It is the least abundant and most toxic of the elements known to be essential for mammals. Average abundance in the earth's crust is 0.05 ppm and in sea water it is 0.00009 ppm.

World production in 1976 was 1,364 metric tons of which the United States consumed 486 metric tons (U.S. Bur. Mines 1978).

Se usage in 1976 in the United States was 35 percent for electronic and photocopier components, 30 percent for glass manufacturing, 25 percent for chemicals and pigments and 10 percent for other uses. Industrial chemicals include cadmium sulfoselenate used widely for yellow and red pigment in plastics, paints, inks and enamels. It is also used for dandruff treatment and other pharmaceutical preparations.

Sources and Environmental Contamination

In addition to pollution from industrial and other emissions, selenium occurs in coal (3.0 ppm) and Sax (1974) estimated the mobilization of Se into the atmosphere from coal combustion at 420 tons per year, with an additional 30 tons from oil. Selenium efficiently passes through the combustion process in coal and appears on the surface of respirable particles emitted from the stack. Not much is known about the effects of release of Se from fuel comsumption. Selenium in river flow from weathering mobilization was estimated at 7,200 tons per year.

Sources and Pathways to Biological Organisms

Selenium occurs naturally in concentrated form in some regions and in very low amounts in other areas, resulting in excesses and deficiencies depending on the region.

The major sources and pathways of Se to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring Se in the soil and irrigation water.

        - b. Fallout from coal and oil and waste combustion and from industry.
        - c. Se in sewage sludge fertilizer and compost.
    - 2. Plant contamination from the air.
        - a. Combustion of coal oil and refuse.
        - b. From industry.

- b. Animals
    - 1. Terrestrial
        - a. From eating plants or animals containing Se.
        - b. From breathing air or drinking water containing Se.

    - 2. Aquatic
        - a. From naturally occurring Se in water.
        - b. From eating plants and animals containing Se.
        - c. From runoff contaminated by fallout from coal, oil and industry.
        - d. For filter feeders from Se contaminated organic and inorganic particulate matter.

Tin

Abundance and Use

Tin is not ubiquitous on the earth's surface and is not commonly found in plants, animals and soils. It is concentrated in several minerals, especially in cassiterite, which occurs mainly in low grade alluvial deposits, where it is obtained by placer mining. The concentration of tin in the earth's crust is 2.0 ppm and in the ocean is 2.0 ppb.

The world production of tin in 1968 was 227,000 tons and in 1976 was 225,240 metric tons. The estimated demand for year 2000 is 290,000 tons. Tin recovered from secondary sources, and scrap accounts for about 30 percent of total consumption. Over 23,000 metric tons from scrap was used in the United States in 1968. Tin consumption in the United States in 1976 was 61,934 metric tons (U.S. Bur. Mines 1978). The estimate for the United States demand in year 2000 is 101,000 to 180,000 metric tons and the cumulative demand for primary tin from 1968 to 2000 is estimated at 7.5 million tons (WHO 1976b).

Tin is used in tin and terne plate, solder, babbitt, bronze, pewter, plastics and tin chemicals. Tin compounds are used for making plastics, textile additives, bactericides, fungicides, herbicides, acaricides, miticides, slimicides, insecticides, anthelminitics, anti-fouling paints and wood preservatives.

Sources and Environmental Contamination

Organotin derivatives account for the fourth largest production of organometallics amounting to over 2,000 tons per year. These are disseminated into the environment mainly as biocides due to their very high toxicity. It is estimated that 2,000 tons is now used and over 5,000 tons of tin will be used in plastics by year 2,000 (WHO 1976b).

Tin is also found in coal and oil and when burned, contributes to the environment. Tin smelting also causes local pollution. These contribute about 300 tons, with total air pollution of tin caused by man estimated at 30,000 tons/year.

Sources and Pathways to Biological Organisms

High natural levels of tin occur in only a few places in the world such as Malaysia, Thailand, Indonesia, Nigeria, China, Bolivia and a few other countries. Dredging, mining and smelting cause local pollution. Most of the tin pollution is caused by activities of man.

The major sources and pathways of Sn to biological organisms are:

a. Plants
  1. Uptake by roots from soil.
    a. In Sn areas in some countries.
    b. From soil contaminated from mines, dumps, and smelters.
    c. From use of biocides and phosphate fertilizers.
  2. Plant contamination from air.
    a. Incineration of coal, oil and plastics.
    b. From fungicides, herbicides and pesticides on plants.

b. Animals
  1. Terrestial
    a. From eating plants containing Sn (local).
    b. From drinking contaminated water or breathing contaminated air (local).
    c. From insecticides, herbicides and other biocides.
  2. Aquatic
    a. Naturally occurring Sn in seawater.
    b. From mine and placer waste, smelters, dumps, and incineration of coal, oil and plastics.
    c. From use of biocides especially antifouling paints.
    d. From ingestion of algae and marine organisms.

Vanadium

Abundance and Use

Vanadium is widespread and about as plentiful as zinc or nickel, but is never highly concentrated. Carnotite and titaniferous magnetite may contain up to 3 percent V_2O_5. It is found in uranium ore and in phosphate rock deposits. The concentration is about 135.0 ppm in the earth's crust and in the ocean is about 2.0 to 5.0 ppb.

The world production of vanadium in 1976 was 25,537 metric tons. Vanadium use in the United States in 1976 was 4,650 metric tons and in the chemical industry was 200 to 250 tons (U.S. Bur. Mines 1978). It is used in steel production, as catalysts in polymerization processes, including synthetic rubber and plastics. Vanadium residues from fly ash, slags and spent vanadium catalysts are used in production of vanadium products. Ash from petroleum burners may contain up to 70 percent V_2O_5, and 5 to 18 percent in fly ash.

Sources and Environmental Contamination

The greatest amount of vanadium pollution of the air comes from burning coal and oil. In the United States coal combustion contributed 1,750 to 3,760 tons of vanadium to the atmosphere in 1968. Residual oil combustion emitted 14,000 to 22,000 tons to the air in 1970 (Nat. Acad. Sci. 1974a). The total vanadium air pollution in 1975 in the United States was aobut 20,000 tons. The air pollution in eastern United States is greater due to burning high V concentration oil imported from Venezuela.

Sources and Pathways to Biological Organisms

There are few areas with high concentrations of vanadium but it is common and widely distributed in small amounts. Most of the concentrations of vanadium are caused by man around smelters, phosphate processing plants and especially from combustion of coal, oil and refuse. This atmospheric contamination is mostly in areas where there is heavy residual fuel oil combustion especially in eastern North America.

The major sources and pathways of vanadium to biological organisms are:

a. Plants
    1. Uptake by roots from soil.
        a. Naturally occurring V.
        b. From air pollution fallout on soil and some drainage.
    2. Plant contamination from air.
        a. From combustion of oil and coal.
        b. From incineration of refuse, tires and plastics.

b. Animals
    1. Terrestrial
        a. From eating plants or animals containing V.
        b. From breathing V contaminated air.
        c. From drinking water containing V.
    2. Aquatic
        a. Naturally occurring V in seawater.
        b. From fallout from atmosphere and runoff.
        c. From ingestion of algae and aquatic organisms.

NEEDS AND PRIORITIES FOR BIOLOGICAL MONITORING

The needs and priorities for biological monitoring on a global, regional national or local scale must be clearly defined. This must include both exposure assessment monitoring and surveillance monitoring of the environment and of food organisms. The needs for biological monitoring of each trace metal are defined on the basis of toxicity of the trace element and its most toxic compounds, world production and use, emissions into the air, water and soil, and the degree of hazard to man and his domestic animals. The hazards of ingesting trace metals in food are also defined, and needs to monitor food.

Visualization of the toxic trace element problem (or lack of problem) to man, the geographic area or areas involved and the type or types of biological monitoring needed (or not needed) are presented for each selected trace element based on summarization of all of the data in Section II of this report. Production use and emission data are repeated to help define the problems and the needs for biological monitoring, and the requirements for selecting monitoring organisms.

Another view of biological monitoring needs can be visualized by considering the monitoring requirements of man and his environment. Monitoring needs could be listed as follows:

1. Monitor man
2. Monitor environment of man
    a. The immediate environment -- urban and rural
    b. The general environment
        1. Terrestrial
        2. Freshwater -- rivers and lakes
        3. Marine and estuarine

This also helps to define monitoring needs from the standpoint of the different habitats and types of organisms required.

There appears to be a need for using a few carefully selected biological monitoring organisms for surveillance monitoring of all of the important toxic trace elements on a global scale to determine baselines and trends. The recommendations for no defined biological monitoring program for certain toxic trace elements on a global basis is not in contradiction to baseline global biological monitoring.

Antimony

Antimony is toxic to man, but there is relatively little air pollution in the United States. World production in 1976 was 75,065 metric tons and the United States used 34,581 tons. It is widespread in small quantities, with highest levels in industrial areas from combustion of fuels and refuse. There is no known hazard from food except leachate from containers bearing Sb.

There appears to be a relatively low or no present requirement for biological monitoring on a global, regional or national scale for antimony. Use in the United States is increasing so that the monitoring problem should be reviewed. Any monitoring would probably be local such as around antimony recycling facilities, battery manufacture and disposal, foundry wastes and areas with high fuel and refuse consumption. No food organism monitoring appears needed, since levels in food are usually low. Wherever significant antimony pollution is suspected monitoring should be undertaken, so that biological monitoring organisms will be needed.

Arsenic

Arsenic is toxic, especially arsenic trioxide, arsine and other As compounds. The use of arsenic has decreased greatly in the United States to 4,196 metric tons in 1976 from 23,808 metric tons in 1973. However, much of the use is for agriculture which results in high pollution. Environmental contamination from all sources was about 73,000 tons in 1974. While the dissemination is widespread from pesticide use and coal consumption the major problems are around lead, zinc and copper smelters and one arsenic smelter. There are no known regional gradients of arsenic pollution.

There appears to be a rather low priority need for biological surveillance monitoring of arsenic on a global or national scale. There is a definite need to monitor small regional areas and localized areas around smelters, and localities where arsenic compounds are used in large quantities. Arsenic also occurs in fairly high concentrations in certain foods and may constitute some hazard especially in shellfish. Fortunately this contained arsenic is not readily absorbed by man, but arsenic in certain foods should be monitored.

Beryllium

Beryllium is the most toxic trace element of the 14 selected for study. Its use is relatively small (519 tons in 1976 with 148 tons emitted to the atmosphere of which 133 tons was from coal combustion). Projected U.S. consumption in year 2000 is 1,500 metric tons.

There does not appear to be a defined requirement for biological monitoring on a global or national scale. Any need for biological monitoring would be local around beryllium mining, processing or manufacturing areas, and perhaps in areas of high coal combustion. There is little or no need for monitoring foods for Be. There are presently no known bioconcentrator of Be, and it is poorly absorbed in the intestinal tract. Beryllium is so highly toxic that monitoring requirements should be reviewed periodically especially as use increases.

Boron

Boron is not toxic (except borane) and does not constitute a health problem from food sources and probably not from atmospheric pollution. Although very large amounts are produced and used, there is little hazard. There is about 10,500 tons of boron mobilized into the air per year.

There appears to be no need for biological monitoring on a global or national scale and no known need for local monitoring. There is also no known need to monitor foods for boron.

Cadmium

Next to lead, cadmium constitutes the greatest hazard to human health of the 14 trace metals studied. It is highly toxic to man. World production in 1976 was 18,594 metric tons and United States consumption 5,886 metric tons. Projected world demand for year 2000 is between 25,000 and 49,500 tons.

The annual emission of cadmium to the environment in the United States for 1974-1975 was 1,800 metric tons per year with 359 tons from extraction, refining and production, 125 tons from electroplating, 494 tons from consumption and disposal and 151 tons from coal and oil combustion and other sources. About 300 tons are airborne emissions, 25 tons waterborne, and 1,500 tons land-destined wastes. Cadmium use is primarily dissipative, and the forms used are fairly stable and may therefore accumulate.

Cadmium pollution is relatively local around zinc mining and smelters, steel industry, industry such as electroplating and pigments and combustion of wastes, coal and oil and use of phosphate fertilizers and detergents and other sources. Cadmium also constitutes a hazard from food contamination (including from leachates).

There is a definite need for some global and national scale surveillance monitoring, mainly to discover and confirm increases in local or industrial populated regional areas and to show trends. There is a major requirement for biological monitoring organisms for exposure assessment monitoring of local areas with high cadmium pollution. Biological monitoring of various foods is required.

Chromium

Chromium has some toxicity especially in the hexavalent form. An enormous quantity of chromium is produced, 4,203,900 tons for the world in 1968. The United States used 284,000 tons of Cr in 1976. About 16,463 tons of Cr was emitted to the environment in the U.S. in 1970. No harmful effects on the health of man or animals are known to have resulted from the presence of chromium in the ambient air or in public drinking water at current concentrations (Nat. Acad. Sci. 1974). Because some chromium compounds have caused serious health problems in man through industrial exposure and because the hexavalent compounds are irritating and corrosive to tissue and are highly oxidative, the role of chromium in the environment requires careful consideration. Fortunately biological organisms convert hexavalent Cr to trivalent Cr.

There does not appear to be any defined need for global or national biological monitoring of chromium, but there is a need for limited local monitoring of areas around the metallurgical, and refractory and tanning industries, around cooling towers, and in areas of heavy fuel consumption. There is little need to monitor foods since levels of Cr are relatively low and there is no defined problem.

Cobalt

Cobalt has low toxicity to man. The world production was 28,228 tons and United States consumption 8,287 tons in 1976. Environmental contamination in the United States was about 730 metric tons emitted to the air from coal and gas combustion and some additional pollution from paints and chemicals.

There does not appear to be a defined need for global or national biological monitoring of cobalt. Local areas around cobalt industries and in areas of heavy coal combustion may require monitoring. Only specific biological monitoring of foods appears necessary. Molluscs and other marine organisms may have high levels of Co and monitoring of these organisms with regard to human consumption is probably needed.

Copper

There is an extremely high amount of Cu in the environment. World production was 8,083,090 metric tons and use in the United States was 2,206,600 metric tons in 1976. Total man-caused air pollution has been estimated at 200,000 tons/year. However, Cu toxicity to man is low and absorption and storage is regulated by homeostatic mechanisms. Very high levels of Cu are required to cause illness.

There does not appear to be a requirement for global, regional, local or national biological monitoring of copper in the environment. In only very high exposure areas does it appear justified. Levels of Cu in oysters may be extremely high and monitoring of oysters and other foods should be conducted.

Lead

Lead is the most dangerous and important trace metal studied. It is already at toxic levels in cities, in areas with heavy vehicular traffic, and in areas around the lead metallurgical industries. World production was 4,625,790 metric tons and United States consumption was 1,466,470 metric tons in 1976.

The greatest amount of air pollution comes from combustion of the 380,000 metric tons of tetraethyl lead (world use 1973). In the United States 235 972 metric tons was used in 1976 (an increase of 15 percent over 205,311 metric tons used in 1975) which at 70 percent emission to the air totals 165,180 metric tons. Much of the remaining 30 percent is in motor oil, much of which is burned, so that there is about 200,000 metric tons emitted to the air. Smelters and refineries add to the atmosphere about 18,000 tons, incineration of solid wastes contributes 10,000 tons, and coal burdens the air with 3,500 tons. Other sources include lead in paint and lead arsenate pesticides (2,285 tons).

One can visualize lead pollution of North America as a thin blanket with little or none in the northern tundra areas and progressively more southward with large blisters over cities and industrial areas, mines and smelters and increased levels over highways with a major amount from Boston to Richmond and west to Chicago and the midwest. There would be exceptionally high blisters over the lead belt of Missouri, Los Angeles and other areas. The levels would be fairly constant throughout the year since the major amount is from combustion of tetraethyl lead in gasoline which, despite partial use of no-lead gasoline, is increasing based on latest available reports (U.S. Bur. Mines 1978).

This picture of lead pollution then allows a better comprehension of the monitoring problem. It helps to define where biological monitoring organisms should be used for coordinated surveillance monitoring programs as well as the need for integrated exposure assessment monitoring.

There is an urgent, high priority well-defined need for global (especially northern hemisphere) national and regional biological monitoring. In addition, there is an urgent need for local monitoring around man, especially in cities. There is also a need for biological monitoring to determine trends in environmental levels of lead. Furthermore, there is a need to monitor foods, consumed by man and his domestic animals, especially in highly populated and industrialized areas with high vehicular traffic.

Mercury

Mercury is highly toxic in some forms and there is biotransformation of elemental mercury to compounds with higher toxicity. World production of mercury was 8,429 metric tons and United States consumption was 2,241 metric tons in 1976 or a 28 percent increase over 1975. The estimated Hg emission to the air in 1975 was 20,000 tons with 5,000 tons from combustion of fossil fuels, 2,000 tons from smelting ore, and 5,000 tons from phosphate and heating processes. The chloralkali, vinyl plastic and wood pulp industries pollute water but controls have reduced emissions. Sewage sludge may release 1,000 tons of Hg.

There appears to be a limited need for global or national biological monitoring of mercury. There is a need for local monitoring where mercury is mined, processed, or emitted to the environment. In Sweden, Japan and other countries where mercury is used in industry, agriculture and other uses, a national or regional monitoring program is needed. In the United States, mercury pollution appears to be a local or non-regional type of contamination without extensive regional gradients (with perhaps an exception along the heavily industrialized and populated Atlantic coast). Biological monitoring on a limited scale appears to be needed. "Market basket" type surveys in which a great variety of foods are examined indicate that mercury concentration in foods other than meats, fish and poultry products is minimal or non-existent (Battelle 1977). However, monitoring of fish, shellfish, meat and poultry should be continued.

Nickel

Nickel is slightly toxic to humans, but nickel carbonyl is highly toxic. World production was 872,342 metric tons and U.S. consumption 160,350 metric tons in 1976. Nickel emission to the air was 4,859 tons from combustion of fuel oil and 90 tons from coal, 260 tons from the metallurgical industry and 30 tons from other sources for a total of 5,244 tons of Ni into the air.

Nickel pollution is presently considered to be of importance in areas of heavy fuel oil combustion, around smelters, and especially in the nickel industry where occupational exposure is a threat. Present nickel pollution is widespread, but the only hazardous form is nickel carbonyl.

There does not appear to be an important need for global monitoring, but a limited need exists for regional or national biological monitoring of nickel. There is a definite need to monitor local specialized pollution such as around smelters and wastes from nickel plating. Fuel oil combustion products should be studied. Exposure of humans to large amounts of nickel in foods may occur in some areas so that some food monitoring is required.

Studies of mosses in Scandinavia showed an increase in atmospheric Ni related to increased burning of coal. This monitoring should be continued and projections on atmospheric pollution should be made.

Selenium

Selenium is toxic to humans and to domestic animals. World production was 1,364 metric tons and United States use was 486 metric tons in 1976. Selenium air pollution from coal combustion was 420 tons and from oil 30 tons pet year (Sax 1974).

Selenium is the cause of selenosis poisoning of cattle, sheep, and horses. Selenium is naturally abundant in the Rocky Mountains and Great Basin states where selenosis occurs and is a problem to people living in seleniferous areas who consume local food (Schroeder 1974).

There does not appear to be a defined need for global biological monitoring but there are regional and local areas in the world where selenium is abundant and biological monitoring would be of value. This includes the seleniferous area of the western United States. In such areas food monitoring is needed.

Se was not considered to be a significant pollution problem, but a number of areas where further research is needed has been published by the Nat. Acad. Sci. (1976).

Tin

Tin has relatively low toxicity but certain tin compounds such as triethyl tin are highly toxic. World production of tin was 225,240 metric tons and U.S. consumption 61,930 metric tons of which 30 percent was from scrap and secondary sources. Over 2,000 tons of toxic organotins was disseminated into the environment as biocides in plastics. Combustion of oil and coal contribute 300 tons of tin to the air. Total air pollution is estimated at 30,000 tons/year but is not considered to be a real hazard due to the relatively low toxicity of tin. However, organotin is far more toxic and constitutes a higher risk. The most toxic biocides are triphenyl tin acetate or chloride, dibutyltin oxide or laurate, triaryltin compounds and trivinyltin compounds (WHO 1976b).

Tin pollution can be visualized as widespread with few high levels in the United States, with wide dispersal of organotin. Smelted tin is mostly imported except for a smelter in Texas which produces 2 percent of U.S. tin. Tin pollution is not considered to be of much importance to man.

There does not appear to be a defined need for global, regional, or national biological monitoring of tin. Local monitoring of areas with high organotin use should be considered. There is no known need for monitoring food for tin, except in relation to contamination from leachate from tin containers and solders.

Vanadium

Vanadium has low toxicity to man. World production was 25,537 metric tons and United States use was 4,650 metric tons in 1976. The major air emission source is from combustion of residual oil -- 14,000 to 22,000 tons of vanadium in the United States in 1970 and coal combustion of 1,750 to 3,750 tons in 1968. Total air pollution in 1975 was about 20,000 tons.

Vanadium pollution can be visualized as a fairly widespread light pollution occurring wherever residual oil fuels and coal are burned, with a heavier concentration in eastern North America due to combustion of Venezuelan oil. The major concentration occurs from Washington, D. C. to Boston and Ottowa and is much greater in winter due to combustion of heating oils. There is also some vanadium pollution around the steel industry where vanadium alloys and products are manufactured.

There does not appear to be a defined need for global or national biological monitoring since there is little hazard from air or food. Limited regional and especially local monitoring in areas of very high fuel oil combustion may be desirable. The vanadium pollution problem is regional in northeastern North America and it is increasing and is somewhat seasonal; however, little or no biological monitoring of vanadium appears to be required.

SUMMARY

The present needs, requirements and priorities for biological monitoring of selected toxic trace metals have been analyzed in broad terms. Relative needs and priorities for biological monitoring of the trace metals in global, regional or national and local environments have been evaluated. Needs for both exposure assessment and surveillance monitoring including food have been considered (Table 4).

In general, the needs and priorities for biological monitoring agree fairly well with those stated by WHO, EPA and the National Pesticide Monitoring Program, except that this report strongly emphasizes the very high priority and urgency of monitoring lead, especially tetraethyl lead in cities, industrial areas and areas of high vehicular traffic.

Since production, useage and emissions and controls are always changing, these monitoring needs are subject to change. The decrease in mercury emissions and better perspective and understanding of the problem is the reason for recommending decreased needs and priorities for biological monitoring of mercury.

TABLE 4. NEEDS AND PRIORITIES FOR BIOLOGICAL MONITORING

	Environmental Monitoring			
	Global	Regional, National	Local	Food Surveillance
Antimony	0	0	X	0
Arsenic	X	XX	XX	XX
Beryllium	0	0	X	0
Boron	0	0	0	0
Cadmium	X	XX	XXX	XXX
Chromium	0	0	X	0
Cobalt	0	0	X	X
Copper	0	0	X	X
Lead	XXX	XXX	XXX	XX
Mercury	0	XX	XX	XX
Nickel	0	X	XX	X
Selenium	0	X	X	X
Tin	0	0	X	X
Vanadium	0	X	X	0

0 - no biological monitoring (except minimum global baseline surveillance)
X - limited surveillance monitoring only of selected sites or foods
XX - surveillance and exposure assessment monitoring of suspected sites and foods
XXX - surveillance and exposure assessment monitoring of all needed sites and foods in a coordinated program

The review of toxicities, production and use, emissions, sources and pathways to plants and animals for each selected trace metal has been of great value in ascertaining the biological monitoring requirements and priorities in selecting monitoring organisms.

SECTION III

BIOLOGICAL MONITORING

Our preoccupation and obsession with technology and instrumentation to improve or maintain our quality of life often makes us overlook the best possible monitoring system — life itself. Living organisms have been used to monitor environmental quality dating back to use of the miners' canary a century ago. We should not forget that we share the earth with many types of life upon which we are completely dependent for survival. Further, these forms of life are strictly dependent upon the habitability of our environment and are therefore unique and very valuable indicators and monitoring organisms to use for evaluating the environment. Our task is to select those forms of life and methods which can be used most effectively for biological monitoring.

VALUE OF BIOLOGICAL MONITORING

Bilogical monitoring is a broad concept. It consists not only of analyzing levels of pollutants in organisms, or studying toxic effects of chemicals in specific situations, but also includes ecological evaluation. Biological organisms continuously integrate their response through time and react to all synergistic and antagonistic effects of combined pollutants and/or stresses. They provide a moving time-averaged value for the relative biological availability of a pollutant at the site studied. Biological monitoring organisms provide important pollutant exposure data and give actual responses, instead of predicting biological responses and effects from physical and chemical measurements of the environment.

Living organisms act as continuous early warning monitoring systems that provide man with the first alarm of danger in the environment, just as the miners' canary warned of dangerous methane in mines. Death and illness of herons, fish, shellfish and crabs preceded the deaths of over a hundred human beings from mercury poisoning in Minamata and Niigata Bays in Japan (Matida and Kumada 1969). The mercury problem alarm was sounded in Sweden in the middle 1950's when populations of the yellow bunting catastrophically declined, followed by deaths, reproductive failures and population declines with high body concentrations of mercury of seed-eating pheasants, partridges, pigeons, finches and also raptorial birds (Holt 1969). Deaths of zoo animals in New York City and of horses in California and Wales warned of high levels of lead in the atmosphere. Deaths and egg shell thinning of hawks, pelicans and many other birds warn of high levels of biocides in the environment. Decreases in populations of wildlife, elimination of species, increases in the number of rare and endangered species, and poor condition and pathological damage in plants and animals warn of decreased quality of the natural environment.

Plants and animals can serve as biological monitors for showing changes in levels of pollution and environmental contamination, and as reference points in determining direct or indirect effects on man. They act as sensitive indicators, as recorders of environmental conditions, as bioaccumulators, and as bioassay organisms. Use of biological monitors offers great potential for detecting, in the early stages, changes and undesirable trends in the ecology of an environment. They can also be used to help determine the effectiveness of control measures put into operation.

Plants and animals may be continually exposed and act as long-term monitors. They can also provide a representation or historic record of the environmental conditions that have prevailed, and are graphic records of the time of occurrence and levels of chemical pollutants. By analyzing certain organisms it is possible to tell which poisonous materials were or are present. Study of museum specimens can also indicate the amounts of certain contaminants that were present many years ago. Comparison of the levels of elements or organisms in the same locality over a period of years provides an historic record showing trends in levels of pollutant trace elements.

There is public concern for the effects and biochemical changes resulting from long-term low-level exposures to toxic trace metals. The capability of biological organisms to accumulate and concentrate these metals in the environment greatly assists research on environmental pathways and exposure assessment directly related to man (Morgan and Bretthauer 1977). In all types of biological monitoring it is necessary to concurrently make critical physical and chemical measurements of levels of trace metals in the environment.

In summary, biological monitoring organisms provide many advantages because they can be used to:

1) Provide early warning to man and help discover and identify toxic trace element pollutants in the early stages of environmental contamination. This is especially true for trace elements that occur in very low levels in the environment.

2) Identify impact areas and sites of accumulation, and measure environmental gradients of levels of trace elements from sources.

3) Elucidate critical pathways of pollutants to man in his water, air and particularly food (since plants and animals are his food).

4) Establish baselines and integrate levels of trace elements over geographic areas.

5) Help show trends and rates of changes in levels or toxicity over time.

6) Integrate biological exposure of toxic trace elements with physical and chemical measurements in the environment.

7) Provide continuous monitoring systems over time correlated with many other factors in the environment.

8) Evaluate effectiveness of control measures.

CONCEPTS AND TYPES OF BIOLOGICAL MONITORING

The concept of biological monitoring includes the use of man to assess exposure to toxic pollutants. In addition, selected biological organisms can be used in place of man for exposure assessment and especially surveillance monitoring.

Biological monitoring can be conducted using two fundamentally different but complementary methods. The first method is to measure the accumulation or concentration of toxic trace metals in selected monitoring organisms. This allows less expensive and simpler analyses than extensive direct environmental measurements, and allows fewer measurements since the organisms provide continuous moving time-averaged concentrations. The second method of biological monitoring is the measurement of impacts or effects of toxic trace elements on organisms or on populations and communities of organisms. This measures the combined effects of all pollutants, and in addition, the impacts of environmental factors such as temperature, oxygen content, nutrients, sunlight, and water availability.

In this report, only biological monitoring using accumulator and concentrator organisms is considered. Biological monitoring of impacts and effects of toxic trace metals is briefly discussed for comparative purposes only.

Monitoring of Concentrations of Trace Metals in Organisms

Measurement of the concentrations of toxic trace elements in biological organisms identifies the type of trace element and directly measures the exact concentrations of residues of the elements accumulated or concentrated in the organisms. Direct chemical measurement of the accumulations or concentrations in organisms is especially effective for trace elements that occur at very low levels in the environment at the threshold of measurement capability.

Processes that are involved in determining the concentration level of a trace element in a plant or animal include bioaccumulation and bioconcentration in the organism, biomagnification and biominification at different trophic levels in food chains, and biotransformation of the chemical form of an element in organisms.

Bioaccumulation and Bioconcentration

Bioaccumulation and bioconcentration of trace elements are the main processes by which the elements are taken into and stored in plants and animals.

Bioaccumulator organisms take up, accumulate and store specific pollutants so that the organisms' intake is greater than the output. The pollutant may be absorbed and stored internally or may be accumulated on external surfaces or both. In the case of lead accumulation on leaf surfaces, much of this may be washed off by rain or with detergents.

Bioconcentrator organisms selectively accumulate, and concentrate the specific pollutant by sequestering it into certain organs or tissues such as teeth, claws, hair, feathers, skin, bone, kidney, liver or other organs. Some toxic substances are concentrated in very high quantities in specific organs and do not appear to affect the organisms; however, if minute quantities are introduced into the blood system they may be killed rapidly. Examples of bioconcentrator organisms are tunicates which sequester extremely high concentrations of vanadium in special vanadocyte cells, or oysters which sequester very high concentrations of copper causing "greening".

A general summary of the relative accumulations of trace elements for plants and animals is shown in Table 5. This shows only relative relationships and there are many exceptions. Better summary comparisons can be made by referring to tentative baseline averages and maximal levels of trace elements in Tables 11 to 26.

A quantitative measurement of the relationship between the level of a trace element in the organism compared with the level in the environment is the concentration ratio. This is usually determined in aquatic habitats since it is easier to quantitate the levels of pollutants in the aquatic environment. A definition for aquatic habitats is: "Concentration Ratio is the ratio of the concentration of an element or radionuclide in an aquatic organism or its tissues to that in the surrounding water under equilibrium or steady state conditions" (Thompson et al. 1972). This term is also used for plants in comparing the concentration in a plant with that in its soil. Direct contamination from the air may be a confounding factor. Concentration ratios of trace metals in edible tissues of invertebrates and fish are shown in Table 6 for both marine and freshwater habitats.

Concentration ratios have been widely used to compare levels of trace metals of organisms at all trophic levels directly with the levels in the water. Unfortunately, this has contributed to misinterpretation of the data to "prove" biomagnification in each trophic level of food chains.

Biomagnification and Biominification

Biomagnification of pollutants in organisms is well known and abundantly used in the literature. Biominification, which is very important, has not been properly described nor its significance evaluated. It is pointed out that biominification is important for many of the trace metals especially in the higher trophic levels. The causes or reasons for this dilution process are given and the importance to humans is pointed out.

Biomagnification is the increase in concentration of trace elements(s) in organisms with increasing or higher trophic levels in food chains. This trophic level magnification signifies that the concentration of the trace element in higher trophic levels is higher in the predator than that in the prey species. For biomagnification to occur, it is necessary that the prey or food organism contain a trace element in the edible or digested parts of the

TABLE 5. RELATIVE BIOACCUMULATION AND BIOCONCENTRATION OF TOXIC TRACE METALS

	Mammals, Birds and Fish	Molluscs, Crustacea, Lower Animals	Higher Plants	Mosses, Lichens and Algae
Antimony	x	x	x	x
Arsenic	xx	xxx	xxx	xx
Beryllium	x	x	x	x
Boron	x	xx	xxx	x
Cadmium	xxx	xxx	xxx	xxx
Chromium	xx	xxx	xxx	xxx
Cobalt	x	x	xxx	x
Copper	xxx	xxx	xxx	xxx
Lead	xxx	xxx	xxx	xxx
Mercury	xxx	xxx	x	x
Nickel	xx	xxx	xxx	xxx
Selenium	xx	x	xxx	x
Tin	xx	x	xxx	x
Vanadium	x	xxx	xx	xx

Bioaccumulation Scale:
x - low or limited
xx - moderate
xxx - high to very high

organism. The trace element must be in a form which is absorbed to some degree. Furthermore, the trace element must be retained and stored with a sufficiently long biological half-life to permit accumulation. The first accumulation usually occurs in microorganisms or plants at the base of the food chain. These are fed upon by filter feeders, herbivores and grazing organisms, which are in turn fed upon by predator and scavenger organisms up to the highest trophic level predatory organisms, which may be carnivorous mammals, birds, reptiles or fish, or scavenger organisms (Table 7). The

TABLE 6. CONCENTRATIONS RATIOS OF TRACE METALS IN EDIBLE TISSUES OF INVERTEBRATES AND FISH (x 1,000 ppm)

	Marine		Freshwater	
	Invertebrates	Fish	Invertebrates	Fish
Antimony	0.005	0.04	0.01	0.001
Arsenic	0.333	0.333	0.333	0.333
Beryllium	0.2	0.2	0.01	0.002
Cadmium	50.0	3.0	2.0	0.2
Chromium	2.0	0.4	0.04	0.04
Cobalt	1.0	0.1	0.2	0.02
Copper	1.67	0.667	1.0	0.2
Lead	1.0	0.3	0.1	0.3
Mercury	33.3	1.67	100.0	1.0
Nickel	0.25	0.1	0.1	0.1
Selenium	1.0	4.0	0.167	0.167
Tin	1.0	3.0	1.0	3.0
Vanadium	0.05	0.01	3.0	0.01

Source: Adapted from Vaughan et al. (1975)

concept of biomagnification implies that storage of toxic substances in herbivorous and carnivorous animals at lower trophic levels may gradually build up in higher trophic level predators, and may kill or cause toxic effects.

Plants take up metals from the soil through roots or from the air through stomata, or through absorption from the leaf surface. Plants which drop leaves or die contribute to decomposing organisms, which may be eaten by other organisms, and contribute indirectly to higher trophic levels, or the litter may accumulate higher levels of the metal which may then be absorbed by plants. After absorption and transloction, the retained metal is usually distributed in various tissues and organs and/or may be concentrated in specific ones. The retention time is variable and the biological half life may vary from days to years.

TABLE 7. BIOMAGNIFICATION OF TRACE METALS

	Terrestrial			Aquatic		
	Plants	Herbivores	Carnivores	Plants	Herbivores	Carnivores
Antimony		2		18,94	18	
Arsenic		50		49,55,29	55	55
Beryllium	14					
Boron	24,37,66,92					
Cadmium	92,50,12,13,36,40	105,45,66,50,99	105	102,28,29,13,38,39,41,54	28,29	3,86,28
Chromium	27	50		39,57,90,94		
Cobalt				57,75,82,90,94		
Copper		66		90,95,106,29,38,39,54,57,69		
Lead	26,92	66,50,0-50		106,38,39,54,57,61		
Mercury	56	22	64,72,74,22	15,59,60,76,89,	104,15,49,76,89	47,48,73,89,96,23,30,33,34,104
Nickel	58,92			75,90,38,39,54,57,69		
Selenium	85,10,20,35,83	20		2		
Tin	44			57		
Vanadium	8,9			57,90	8,52	

Numbers are reference citations; see page 55.

Biominification is the decrease in concentration of a trace element in organisms with increasing or higher trophic levels in food chains. This is a new term coined here to describe this process.

Biominifiction has been observed in a number of studies of trace elements in food chains and has previously been called "dilution" or "discrimination against the trace element" in the food chain or more frequently has been described as lack of biomagnification.

Biominification will occur a) if the trace element concentration is low in the edible or digested parts of prey or food, b) if the trace element has been sequestered and stored in inedible tissues such as bone, hair, feathers, beaks, nails, claws, antlers or horns, shells or exoskeletons, c) if there is low absorption of the trace metal in the digestive system of the predator, d) if the trace element has been biotransformed from a highly absorbed to a poorly absorbed chemical form (e.g., Cr VI to Cr III), and e) if the half-life retention time of the trace metal in the predator is short. Another factor which may affect the minification process is the presence of other competing metals. If the trace element or compound is toxic it may affect the ability of the organism to grow and carry out normal metabolism resulting in decreased uptake.

The distinction between bioaccumulation and biomagnification is important. In the process of biomagnification there may be a buildup of concentrations of the trace element in each trophic level, resulting in very high toxic concentrations in the top level predators (including man). Bioaccumulation, on the other hand, may be the result of accumulation from ingestion of food and contaminated soil or sediment, and in addition in fish, direct absorption of large amounts of the element may occur in the gills and skin. For some trace elements such as methyl mercury in fish, there is almost unlimited absorption and high retention so that the older and larger the individual, the greater the concentrations of trace element. This makes distinction between bioaccumulation and biomagnification difficult, and makes the decreasing levels observed in biominification all the more interesting or significant.

Biomagnification of trace metals in food chains is commonly accepted as the usual process resulting in predators at the highest levels having very high concentrations. However, study of the literature compiled in Volume 2 indicates that there is either no biomagnification, or a decrease in level for most of the trace metals with increasing trophic levels of the food chain.

In order to determine the importance of these processes with regard to selection of monitoring organisms, a rather comprehensive review was made of all available food chain studies or data showing accurate relationships between trophic levels of food chains (Tables 7 and 8). The number of examples, indicated by the number referring to the literature source, shows the relative frequency and importance of increase or decrease of toxic metals at a trophic level.

For plants, comparisons were made between levels of trace metals in the soil with leaf, stem and other tissue combined. For aquatic plants, comparison was made between trace element level in soil or sediment with

TABLE 8. BIOMINIFICATION OF TRACE METALS

	Terrestrial			Aquatic		
	Plants	Herbivores	Carnivores	Plants	Herbivores	Carnivores
Antimony	66	66	50			16,81
Arsenic	66,92,50	66	7,50		29,0-29, 7,0-79,87	0-79,80, 6,7,0-55, 0-62
Beryllium	14					
Boron	92	66				
Cadmium	12,13,35, 36,40,66, 92,0-99	0-105,66, 99,105	0-50,99	30,102		0-106,62, 68,81,86, 60,31,32, 42,63
Chromium	92,50,43, 44,66,88	66,93,50	0-50			65
Cobalt	4,66	0-66		90,94	53,82	53,82,94
Copper	1,20,66, 70	20		69	69,71,29	60,106, 0-31,0-62, 69
Lead	66,92, 0-50,1, 25,35,36	84,105, 21,25,26	77,0-50, 105,21, 25,46	98	19	106,19,62, 68,98
Mercury	56,66,91	0-66	103,0-103	0-97	0-97	0-71,0-97
Nickel	85,88,92, 1,16,35, 58,70	17			69	0-31,0-62, 69
Selenium	83,85,10, 37,66,78	5,10,66				80
Tin	66,0-44, 101	66				
Vanadium	9,11,35, 52,66	9,66				

Numbers are reference citations; see following page.

References for Tables 7 and 8

1. Timperley et al. (1970)
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rooted plants, and between levels in water with the plant for aquatic floating or sessile non-rooted species. It is recognized that external contamination of leaves (e.g., lead) may bias the data, so that comparisons in heavily air polluted areas were not used. Mosses and lichens were not used for comparison because their trace metals come almost entirely from air pollution.

For animal comparisons, an attempt was made to compare whole body concentrations. In some cases muscle tissues were compared, however, since predators often eat whole animals including the liver and kidney, which may have high concentrations of certain trace elements, this would skew analyses toward biomagnification. Data on trace metal level in prey fish based on whole body minus head were compared by Windom (1972) with predator fish muscle and decreases in certain trace elements were found. This comparison would skew analyses toward biominification and the examples are designated with a question mark in Table 8.

There are many examples of prey with trace metal levels given for the whole body or muscle tissue, but for the predators, trace metal levels were given for hair, liver, kidney, feathers or eggs. These non-comparable types of data are frequently used erroneously by many authors to show biomagnification. Non of these non-comparable data were used in Tables 7 and 8. Other types of organisms excluded for comparison were omnivores or scavengers with unknown trace metal levels in foods or unknown percentages of various foods eaten. Organisms such as oysters and clams which may feed on phytoplankton, zooplankton, sediment and detritus were excluded, except for examples of predation on the molluscs. Most soil and litter feeders such as earthworms were also excluded.

The trophic levels included for both aquatic and terrestrial habitats were a) the trophic level from soil or water to plants, b) the herbivore trophic level of consuming algae, higher plants, or plant products, and c) the carnivore trophic level of consuming zooplankton and other invertebrates or fish or smaller birds and mammals. This last category covers several trophic levels (1st, 2nd and 3rd order carnivores).

The examples for biominification are shown in Table 8. Where there was no significant change in level of trace element 0- and the reference number was used. The examples are summarized in Table 9.

For terrestrial organisms Tables 8 and 9 show that there is frequently biominification of trace level between soil and plants for all 14 trace elements. There are also examples of herbivore biominification for all trace metals except for Be, and no change for Co and Hg. Biominification from prey to carnivore occurs for Sb, As, Cd, Pb and Hg and no change for Cr.

TABLE 9. RELATIVE IMPORTANCE OF BIOMAGNIFICATION AND BIOMINIFICATION IN FOOD CHAINS

	Terrestrial			Aquatic		
	Plants	Herbivores	Carnivores	Plants	Herbivores	Carnivores
Antimony	-	+ -	-	B	+	M
Arsenic	M	+ -	M	B	+ 0 M	+ 0 M
Beryllium	+ -					
Boron	B -	-				
Cadmium	B M	B 0 M	+ 0 -	B M	B	B 0 M
Chromium	+ M	+ M	0	B		-
Cobalt	M	0		B	M	M
Copper	M	+ -		B -	M	0 M
Lead	B 0 M	B 0 M	0 M	B -	-	M
Mercury	+ M	+ 0	B 0 -	B 0	B 0	B 0
Nickel	B M	-		B	-	0 -
Selenium	B M	+ M		B		-
Tin	+ 0 M	-		+		
Vanadium	+ M	M		B	B*	

B - biomagnification reported two or more times
+ - biomagnification reported once
M - minification reported two or more times
- - minification reported once
0 - no change in trace metal level
* - tunicates

For aquatic habitats biominification occurs for plants from sediment or soil only in freshwater rooted plants for Cd, Cu and Pb and no change for Hg. For herbivores decreases occur for As, Co, Cu, Pb and Ni, and no change for Hg. For carnivores decreases occur for Sb, As, Cd, Co, Cu, Pb, Ni and Se and no change for Hg.

Examples for biomagnification are shown in Table 7 and summarized in Table 9. For terrestrial habitats, increase in levels of trace elements from soil to plants occurs for Be, B, Cd, Pb, Hg, Ni, Se, Sn and V. For herbivores, increases take place for Sb, As, Cd, Cr, Cu, Pb, Hg and Se. For carnivores, biomagnification occurs only for Hg and Cd.

For aquatic habitats there are many examples of increase in level of trace metals from sea water to algae for all elements except Be and B. For herbivores, increases occur for Sb, As, Cd and Hg. The enormous increase in V by tunicates, bryozoa and holothurians occurs in sessile animals that take in V from water and probably sediment and plankton. From prey to carnivores, an increase occurs for Cd and Hg, and for one case for As.

In summary (Table 9) we see that for terrestrial organisms there is usually biominification of trace elements from soil to plants, and some examples of increases, for herbivores there is decrease for 11 metals and increase for eight. However, from prey to carnivore there are decreases for five metals, but increases only for Hg and 1 example for Cd.

For aquatic habitats, there is decrease from soil or detritus at the bottom of freshwater lakes or streams or water to plants (only Cd, Cu, and Pb), but there is a major increase from seawater to plants for all metals but Be and B. This is where most of the biomagnification of trace metals occurs in food webs and food chains. There is some decrease in levels of trace metals for aquatic herbivores (As, Co, Cu, Pb and Ni) and increases for As, Sb, Cd, Hg and perhaps V. However for aquatic carnivores decrease of levels of trace metals from prey to predator is the usual or most common process. This occurs for all metals but Be, B, Sn and V. The most interesting data are the examples of increase in predators which occurs only in Cd, Hg and in one case for As.

This comparative analysis shows that there is important biomagnification in the lower food chain trophic levels, and at higher levels only for Cd and Hg. For these two elements, there is an increase of levels of trace metals in higher order predators with increase in size and age. Williams and Weiss (1973) from a detailed study of amounts of mercury in a trophic pyramid, concluded that mercury is accumulated with time in long-lived animals and that the food chain accounts for very little biomagnification of these levels. Increase of levels of Hg with age and size would account for the very high levels of Hg in the largest tuna, swordfish, marlin, seal, sea lion and walrus, without postulating any Hg pollution of the open ocean. For the sea mammals, local estuaries or coastal pollution may have some effects.

In 1971, Stickel (in Nelson et al. 1971) stated, "the traditional food-chain buildup may not occur with mercury. Hannerz (1968) found that uptake by animals was not related to trophic levels, but to such factors as metabolic rates and food habits. It is true that predators usually contain more mercury than their prey, but levels can be high near the base of the food pyramid."

The bioconcentration of metals into bone, hair, feathers, hoofs, claws, horns, shells, tests, exoskeleton, leaves and fruit can result in decrease of transfer from one trophic level to the next. After making food chain studies around a mine complex, Roberts and Johnson (1978) stated, "the biological implications of heavy metal pollution are not necessarily related directly to the abundance of such contaminants, but rather to their transference potential and differential mobility within terrestrial ecosystems."

The popular and classic text book description of buildup of trace metals in food chains and webs in the food pyramid is thus seen to be partly erroneous. There is buildup of levels of trace metals in the lowest trophic levels in aquatic habitats and in invertebrates, especially molluscs, but the classical biomagnification from prey to predator more often results in a decrease in level of trace metal. The high levels of mercury and cadmium in older larger predators may result mostly from long-term bioaccumulation.

Omnivores and Scavengers

In addition to predators, there is another very important group of organisms to consider. These are the omnivores and especially scavengers which provide important links in the food chains. Scavengers may feed on organisms of all trophic levels, including even the highest level and older predators. Some scavenger organisms have been found to contain high levels of certain trace elements and they offer an attractive potential for use as biological monitoring organisms. Vultures, crows, fish crows, hooded crows, ravens, jackdaws and magpies and gulls often contain high levels and should be considered for use as biological monitoring organisms. Other scavengers such as ants showed surprisingly high levels of lead, and scavenger aquatic organisms such as crabs and crayfish have high levels of some trace elements. In addition to feeding on the remnants of higher level predators, scavengers feed on dead animals which may have been weakened or killed from the effects of toxic metals. They are therefore organisms that would be quickly exposed. Many scavengers are abundant or are pest species and may be used for monitoring without danger to population levels. Omnivorous scavenger species are therefore considered in selection of biological monitoring organisms.

Biotransformation

Biotransformation of trace elements and their compounds is an important process, especially methylation, or change of valence of the element resulting in changes in solubility, permeability, toxicity, and retention. These changes may have great effect on the transfer of the trace elements in the food chain or the toxicity of the element which may be consumed by man.

Mercury is relatively insoluble, is poorly absorbed and not well retained. When various microorganisms cause methylation from elemental mercury to methyl mercury, the highly toxic compound has higher solubility, permeability and retention in a predator organism.

Some of the known biotransformations are listed in Table 10. There are probably many others which are as yet unknown which may have important biological significance.

Biological Effects Monitoring

In this type of monitoring the impacts or effects of the pollutant on biological organisms are measured rather than the presence of the pollutant itself. It is important to measure or monitor these effects to help answer the question of what do the levels of a trace metal in an organism mean. However, this is extremely difficult and there are many problems, especially due to the combined effects of the many other components of the environment which often outweigh the effects of a single pollutant unless it occurs at very high levels and is extremely toxic. Even the combined effects of high concentrations of several trace metals (e.g., from a smelter) may not show any effects in comparison with effects from sulfur dioxide or other toxic pollutants.

There is an enormous literature in this field and many attempts have been made to quantitate and standardize various methods and techniques. Various indices have been proposed, which are based almost entirely on changes due to many complex environmental factors acting together. Some of these measure the effects of addition of sewage with increased eutrophication. There are, however, some species which are highly sensitive to specific toxic trace metals and these may offer promise if selected and used carefully. The range of response of living organisms to specific pollutants is great and results in a wide range of effects. This is the basis for defining various types of monitoring organisms.

Sentinels, Detectors, Indicators and Bioassay Organisms

Monitoring of biological effects covers a broad range of effects which may include a slight change in behavior of an animal or wilting of a plant. Certain organisms may be used as bioassay or bioreagents. Monitoring can also include mortality and species diversity changes in communities. Highly sensitive species may be used as sentinels, or deaths of wildlife may be used as an early warning system. Many factors such as climatic, biotic and other environmental factors than the specific pollutant being monitored, can cause "effects" especially in causing population changes, and species diversity. The various levels of effects are listed as follows:

1) Non-lethal effects -- a) change in behavior or performance, b) change in physiology, illness, decreased leaf turgor, c) decrease in growth rate, stunting, change in enzyme function, d) decrease in photosysthesis, e) pathology and necrosis, f) mutation, g) decreased reproduction, h) effects on progeny.

2) Lethal effects -- a) low level, long-term or chronic effects resulting in death, b) lethal effects on progeny, c) decrease in egg shell thickness and no reproduction, d) sudden, violent or rapid death.

TABLE 10. BIOTRANSFORMATION OF TRACE METALS AND THEIR COMPOUNDS

	Biotransformation	Authority
Antimony	------	------
Arsenic	--As^{III} to methyl arsine, to As^{V} --Toxic As^{III} to low toxicity organoarsenical --Organo As to methyl As	Ansul Co. (1971) Wood (1974) Klumpp and Peterson (1979)
Beryllium	------	------
Boron	------	------
Cadmium	--Forms coordination complexes with a variety of ligands	Wood (1973)
Chromium	--Toxic hexavalent Cr^{VI} changed to low toxicity trivalent Cr^{III}	Mertz (1969)
Cobalt	-------	------
Copper	-------	------
Lead	--Tetraethyl lead changed to Triethyl lead and some Pb	Friberg (1977)
Mercury	--Hg changed to toxic methyl Hg --Methyl Hg to Hg	Jensen and Jernelov (1969) Spangler et al. (1973)
Nickel	------	------
Selenium	--Selenite and selenate to Se and selenoorganics --Se synthesized to unusual selenoamino acids	Muth and Binns (1964) Versar (1975) Peterson (1971)
Tin	--Tetraethyl tin metabolized to triethyl tin --Triethyl tin transformed to monoethyl tin in gut	Friberg (1977)
Vanadium	--More toxic V^{V} is common in nature but V^{III} stored in tunicates	Levine (1961)

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3) Genetic Resistance. Many species develop increased resistance to chemicals after several generations of exposure and selection.

Many of these effects and particularly the lethal effects produce changes in species populations. When a species population decreases or is eliminated it will be replaced by other species causing community changes (unless the pollutant level is too high). There will also be changes in various indices and species diversity, which may be related to various environmental changes or combinations of factors and pollutants.

Organisms suitable for biological effect monitoring have been categorized by Jenkins (1971) in the following categories:

(1) *Sentinels* -- Highly sensitive organisms introduced into the environment as early warning devices to give an alarm of an approaching or presently dangerous situation.

Sentinel organisms such as the previously mentioned "mine canary" have been used by man as a warning where death or incapacitation of the canary indicated a dangerous concentration of invisible, odorless, methane gas. To warn of an epizootic of yellow fever in jungle areas, "sentinel" captive monkeys are put in the forest and when they become sick and die, man is warned of the danger of the virus.

Sentinel organisms are selected on the basis of being highly sensitive to specific pollutants, and exhibiting definite responses such as pathology, identifiable physiological or behavioral changes or death. It is essential that the sentinel organisms be grown and exposed under controlled conditions to allow adequate interpretation of the responses to contaminants. An understanding of environmental interactions can be used to produce a wide range of sensitivity in monitoring organisms.

In air pollution warning studies, many species of plants have been used as sentinels. To detect ozone, a sensitive strain of tobacco plant (0.05 ppm/2 hours) and white pine (0.06 ppm/2 hours) have been used.

(2) *Detectors* -- Individual species occurring in the environment that show a measurable response (such as pathology, mutation, death, change in physiology or reproduction) to pollutants or to environmental changes.

Detector species have been used to quantify the levels of a pollutant in an area. Lichens are known to be specifically sensitive to SO_2 at known levels, and by mapping the absence of certain species of lichens around a source, fairly accurate isodose lines can be drawn. Some plant and animal species are specifically sensitive to toxic trace metals and some organisms have been used to identify them.

(3) *Indicators* -- are specific species of organisms whose presence indicates probability of pollution or of other dangerous organisms associated with pollution. The most common example is *Eschericia coli* which is measured to determine the sanitary quality of water and to determine probable presence of other fecal coliform bacteria which may be pathogenic. Different levels

of E. coli count have been standardized with reference to water for drinking, swimming and fishing.

The presence of indicator organisms demonstrates polluted conditions, but their absence does not necessarily mean a clean environment. There is often disagreement on the use of indicator organisms and particularly on the types of pollution they indicate. There are very few biological organisms that are specific indicators of toxic trace metals. However, some plants are known to indicate the presence of certain trace elements e.g., lead plant for lead, or "primary selenium indicators" such as Stanleya which is restricted to seleniferous areas.

(4) Bioassay Organisms -- Selected organisms used as bioreagents to detect or monitor the presence, effects and/or concentration of toxic pollutants. The organisms may be indigenous or introduced test species and may be highly sensitive or resistant.

Bioassay is used extensively and the data are usually obtained with reference to humans, but exact extrapolation from plant and animal test organisms to humans is difficult and frequently subjective.

In bioassays there is a requirement to standardize all of the test conditions including the dosage, route of entry or exposure, time, and particularly the bioreagent or test species with regard to nutrition, disease, and environment. It is often necessary to establish human dosage data by extrapolation from a number of species of test organisms. The use of bioassay to determine the toxicity of a pollutant is an effective and accurate method of assessing potential danger.

Use of biological bioassay organisms for toxic substances particularly in aquatic media has been rather fully reviewed by WHO. The response parameters used were: acute response tests, behavioral change, physiological changes, biochemical (and histochemical) change, ecological change, embryological (and regenerational) change, growth change, histological change, and perception by humans and by aquatic organisms. It was concluded that knowledge of bio-assay methods and their application is now sufficiently advanced to permit recommendations as to standard procedures for bioassays of trace element contaminants. Implementation of an international program of standardization was recommended to include selection of: 1) specific bio-assay methods, 2) test organisms stocks and their culture methods, 3) reporting procedures including units of measure and 4) periodic revision of the program based on most recent data. This program would contribute importantly to unifying the widely scattered and as yet largely uncoordinated studies directed towards elucidating the biological effects of enviromental contamination.

Multi-parametric analytical procedures have been developed in the United States using a range of bioassay organisms with different tolerance and sensitivity ranges. The goldfish Carassius auratus and the entomostracon Daphnia magna were used as standard test animals under controlled conditions. The goldfish is relatively resistant to poisons, injury and anoxemia, while Daphnia is more sensitive even than trout, so that the two test animals provided an effective range of sensitivity. The diatom Nitschia linearis was used as a standard organism, also insects, snails, and fish. The organisms are acclimated to the laboratory conditions and exposed to contaminants under controlled conditions. Snails were exposed to pollutants and after failing to respond to stimulii, were returned to uncontaminated rearing water, and if not recovered in 48 hours were determined to be dead. In Europe the fish *Lebistes reticulatus*, an isopod *Asellus aquaticus*, a mollusc *Planorbis corneus*, and an oligochaete *Enchytraeus albidus* were used to provide a comprehensive, multidimensional picture of toxicant effect. These were all reared in the laboratory with known background and freedom of exposure to toxicants. A minimum of apparatus and technicians to observe behavioral and other effects were used.

In aquatic tests two methods are used, a) static bioassay in which a test solution is not changed during the period of exposure, and b) the flow-through bioassay in which the test solution is renewed continually. Toxicity data for flow-through tests are reported as median tolerance limit (TL_m).

Dosages may be given as a high single dose, or as low doses over a period of time. Aquatic organisms may be tested as above or exposed or grown in the water. In static tests the organisms are exposed to, or take up just the amount of material in a container. In flow through tests the test organisms are exposed to the same amount of material continuously.

Test organisms are often selected on the basis of economic importance, sensitivity, and/or importance in the food web of economically important organisms. For example, shrimp are highly sensitive to pesticides and are good bioreagents. In aquatic studies polluted water is tested by using local species of fish as bioreagents. Stocking of streams or lakes with fish is similar to use of sentinel organisms since the effect of contaminants is discernible in the introduced fish. In using living organisms as monitors of aquatic habitats, it is more usual to select certain species of organisms as standardized or reference indicators. The polluted or contaminated water is introduced in a container with the bioassay organisms and the toxicity or effect determined.

Biological Community Monitoring

Biological monitoring of communities or ecosystems involves biological effects on multiple species. Great effort has been expended on developing methods, systems and mathematical analyses of changes in communities due to pollutants. These have involved evaluating the species of organisms present, their populations and changes in population, and their distribution correlated with a large number of physical and chemical factors and changes. Literature in this field is presented by Thomas et al. (1973) in "Biological Indicators of Environmental Quality. A Bibliography of Abstracts."

Some of the various indices which have been developed mainly in aquatic habitats include the following: "Saprobic index," "Species diversity index," "Biotic index," "Sequential comparison index," "Community diversity index," "Distance index," " Pollution index" and such measures as "Biomass productivity" and "Community Ordination." Some of these indices and methods have been quite effective in showing degree and effects of pollution, especially from sewage. However, these measurements are usually too general to be effective in correlating with the specific effects of one or several trace metal pollutants. An exception is very high levels of copper where specific correlations have been made.

Biological community monitoring methodology appears to have limited value for biological monitoring of specific trace metals with our present state of knowledge.

SELECTION OF BIOLOGICAL MONITORING ORGANISMS

Criteria for Selection

The present study is an attempt to define the needs, requirements, and priorities, to evaluate comparatively the available potential monitoring candidate species, to subject them to analysis using strict selection criteria and to select the optimal species and their tissues and organs.

The selection of monitoring organisms is based on the following steps.

a. Compile available data on concentrations of trace metals in biological organisms (Volume 2).

b. Compile and analyze data on use of organisms for biological monitoring of environmental gradients of the trace metals.

c. Develop tentative baseline reference data to show accumulations in non- or low-pollution areas.

d. Analyze species with regard to capability to bioaccumulate or bioconcentrate trace metals in polluted areas.

e. Select species which show the greatest potential for biological monitoring.

f. Select optimal species for biological monitors using clearly defined criteria for selection, taking into consideration the defined needs and requirements.

The comprehensive review of concentrations of toxic trace metals in biological organisms (Volume 2) has resulted in a list of several thousand species of plants and animals. In addition, there is an extensive literature on biological monitoring and many hundreds of species have been suggested or recommended for use by many authors as biological monitoring organisms for a specific or several trace metals. Many of these suggested organisms have valuable potential use for specific trace metals or for specific sites or conditions.

An ideal species for biological monitoring would exhibit unregulated accumulation of a toxic trace element that would be stored or bioconcentrated in a specific organ without showing toxic effects on the organism. Filter feeding bivalve molluscs probably fulfill this requirement better than any others. Even with this type of organism, there are various factors affecting the quantitation for monitoring. These include organism age, weight, size and sex; season; position of sampling; salinity; water temperature; and coexistence of several toxic trace elements (Phillips 1977). Various higher plants and some mosses and lichens also exhibit unregulated accumulation.

An important concept in biological monitoring of levels of toxic trace elements is to use two or more species with different accumulation mechanisms, which would help to eliminate spurious conclusions due to the effects of environmental variables.

The first list of criteria or "ideal characteristics" for selection of biological monitoring organisms for aquatic habitats was presented by Butler et al. (1971):

1. The organism should accumulate the pollutant without being killed by the levels encountered.

2. The organism should be sedentary in order to be representative of the area of collection.

3. The organism should be abundant in the study region.

4. The organism should be sufficiently long-lived to allow the sampling of more than one year-class if desired.

5. The organism should be of reasonable size, giving adequate tissue for analysis.

6. The organism should be easy to sample and hardy enough to survive in the laboratory, allowing defecation before analysis (if desired) and laboratory studies of the uptake of metals.

To these requirements Haug et al. (1974) added the following:

7. The organism should tolerate brackish water.

8. The organism should exhibit a high concentration factor for metals, allowing direct analysis without pre-concentration.

9. A simple correlation should exist between the metal content of the organism and the average metal concentration in the surrounding water.

In addition, Phillips (1977) added:

"To ensure meaningful results from an indicator survey, a major requirment which must be met to avoid spurious conclusions is:

10. That all organisms in a survey exhibit the same correlation between their metal contents and those in the surrounding water, at all locations studied under all conditions. It must, therefore be ensured

> that local environmental variables do not affect the trace metal content of an organism before samples from different environments can be compared."

These strict criteria for aquatic habitats provide excellent background for developing selection criteria for all types of terrestrial and aquatic habitats including plants and animals on a global and/or local basis.

A list of criteria for selection of biological monitoring organisms is presented which may be used for monitoring both terrestrial and aquatic habitats. Factors which have been taken into consideration in making this list include biomagnification, biominification, biotransformation, and use of predators, scavengers and organisms which exhibit unrestricted accumulation of trace metals.

CRITERIA FOR SELECTION OF BIOLOGICAL MONITORING ORGANISMS

1. The organism should accumulate relatively high levels of one or preferably several types of trace metals without being killed or severely injured.
2. They should be common or abundant, their regular collection should not disturb the ecology.
3. Their distribution should be widespread geographically in different biome areas, allowing integration over geographic areas. Individuals should be relatively sedentary or non-migratory.
4. They should be easily collected and handled.
5. They should be of sufficient size to give adequate tissue for analysis; or provide tissue without killing, such as hair, feathers, nails, eggs, milk, leaves, stems or fruit, allowing resampling of the same organism.
6. They should occur in polluted impact areas (critical sources) as well as in undisturbed or unpolluted areas for monitoring environmental gradients of trace metals.
7. The trace metal levels in the organisms should correlate with environmental levels of the trace metals, with minimum effect of local environmental variables.
8. There should be sufficient background data on the organisms, on baselines, accumulation and retention, effects of biological and environmental variables, and experience in monitoring environmental gradients of trace metals.

These criteria are extensive but there are also other factors to consider. These include: a) defined need to monitor, b) monitoring requirements -- area, sites, proximity to man, c) cost, d) man hours, e) frequency of monitoring, f) time span of monitoring, and g) most important, the objectives of monitoring and the actions which can be taken to reduce or eliminate sources defined and monitored by the organisms. These very practical considerations must be considered in monitoring system design and operation.

Use of Organisms for Monitoring Environmental Gradients of Trace Elements

Environmental gradients of trace elements result from emission from a pollution source which may be a point source or a group of sources such as an industrial complex or urban-industrial area. Sources may be more disseminated, as along a highway, or covering a region. Gradients of the trace element may be downwind, downstream, or in a circumferential zoning around the source or sources.

Gradients of the trace elements have been studied by many authors using sites near the source compared with organisms at sites at different distances. Organisms at source sites have frequently been compared with controls at some distances, or at a comparable but unpolluted site. Comparisons have also been made between urban and rural sites.

Biological organisms of many types have been used to measure the concentrations of trace elements at the pollutant site in comparison with different distances and with a control. The results of biological monitoring of the environmental gradients have been compiled for each selected trace element and have been tabulated in Tables 11 to 26. These data have been taken from Volume 2, and from additonal recent publications. The data in these tables on environmental gradients include the scientific name of the organism, the pollution source, the tissue analyzed and the authority. The concentration of the trace element in the organism exposed to the source is compared with the concentration of the control organism at a distance from the source. The increase in number of times of contamination level of the exposed over the control is also shown. Many of the measurements are stated as ranges with an average, and for this comparison the averages were used. When no averages were available, medians were calculated from the ranges (if not too extreme) and used for comparison. These comparisons of exposed versus controls give a suitable estimate of the relative capabilities of the species for monitoring. More precise statistical methods would be required for making exact analytical comparisons.

Antimony

There are only a few examples of biological organisms being used to measure environmental gradients of antimony (Table 11). Of six possible uses, all but one are relatively low level and one is a negative correlation. Guinea pigs fed on swiss chard grown on sludge-amended soil showed a 4.1 X increase in Sb in the adrenal glands as compared with pigs fed on swiss chard grown on normal soil. Limpets showed a small increase in a polluted area versus unpolluted. Crayfish showed a 2.1 X increase in a coal ash basin compared with controls, but midges in the same area showed a -8.9 X negative correlation. Swiss chard grown on sludge-amended soil showed 2.6 X increase over controls grown on normal soil.

The best example of Sb environmental gradient monitoring was shown in wild roses in a gradient downwind from a gold mine and smelter in the North West

TABLE 11. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF ANTIMONY

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Cavia porcellus	swiss chard grown on sludge-amended soil	adrenal	D 9.5	D 2.3	4.1X	Furr et al. (1976)
Patella vulgata	industrial and domestic waste	soft parts	D 0.12	D 0.065	1.8X	Leatherland and Burton (1974)
Procambarus sp.	coal ash basin		2.28	1.11	2.1X	Cherry et al. (1979)
Chironomidae	coal ash basin		2.20	19.50	-8.9X	Cherry et al. (1979)
Beta vulgaris cicla	sludge-amended soil	leaf	D 11.5	D 4.4	2.6X	Furr et al. (1976)
Rosa acicularis	gold mine and smelter	leaf & fruit	D 1.85	D 0.17	10.9X	O'Toole et al. (1971)

D = dry weight, W = wet weight, in ppm

Territories, Canada. The leaf and fruit of roses 0.5 mi downwind compared with 1.9 mi downwind showed a 10.9 X increase over the more distant control.

The experience of using biological monitors for measuring environmental gradients of Sb is limited and more studies are needed.

Arsenic

Comparatively few species of plants and animals have been used to measure environmental gradients of arsenic pollution (Table 12). The arsenic sources include copper smelters, mercury mine, gold mine and refining, leachate from stibnite mine, mine waste, domestic and industrial outfalls and a geothermal area.

While there is an abundance of data on levels of As in biological organisms, there are few examples of biological organisms being used effectively to monitor environmental gradiends of arsenic. Eight species of animals and seven species of plants have been used. Liver of one species of

TABLE 12. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF ARSENIC

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Bos bovis	Cu smelter	hair	W 8.9	W 0.46	19.34X	Orheim et al. (1974)
Bos bovis	Cu smelter	blood	W 0.0258	W 0.0094	2.74X	Orheim et al. (1974)
Bos bovis	Cu smelter	milk	W 0.013	W 0.0075	1.73X	Orheim et al. (1974)
Equus caballus	Cu smelter	mane	D 4.2	D 0.2	21.0X	Lewis (1972)
AMPHIBIA						
Rana temporaria	Hg mine	liver	W 0.195	W 0.047	4.15X	Byrne et al. (1975)
FISH						
Gobius niger	domestic and industrial outfalls	muscle	D 142.0	D 18.0	7.89X	Grimanis et al. (1978)
Gobius niger	domestic and industrial outfalls	liver	D 17.0	D 8.4	2.0X	Grimanis et al. (1978)
Microstomus pacificus	domestic and industrial outfalls	muscle	W 4.12	W 2.43	1.7X	Fowler et al. (1975)
Sargus annularis	domestic and industrial outfalls	muscle	D 9.1	D 2.5	3.64X	Grimanis et al. (1978)
Sargus annularis	domestic and industrial outfalls	liver	D 26.0	D 30.0	-1.2X	Grimanis et al. (1978)

(continued)

TABLE 12. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
CRUSTABEA						
Cancer anthonyi	domestic and industrial outfalls	liver	W 17.29	W 51.02	-2.95X	Grimanis et al. (1978)
ECHINODERMATA						
Strongylocentrus droebachiensis	leachate from stibnite mine	gonad	D 6.0	D 3.3	1.8X	Penrose et al. (1975)
PLANTS						
Agrostis tenuis	mine waste	leaf	D 1,480.0	D 0.23	4,933X	Porter and Peterson (1975)
Calluna vulgaris	mine waste	leaf	D 1,260.0	D 0.30	4,200X	Porter and Peterson (1975)
Picea alba	near Au mine	root	88.0	1.0	88X	Rosehart and Lee (1973)
Potamogeton cheesemanii	geothermal area	whole	D 45.0	D <6.0	7.5X	Lancaster et al. (1971)
Rosa acicularis	Au mining and refining area	leaf and twig	D 138.0	D 15.4	8.96X	O'Toole et al. (1971)
Nitella hookeri	geothermal area	whole	D 182.0	D 13.0	14.0X	Lancaster et al. (1971)
ALGA						
Ascophyllum nodosum	runoff from stibnite mine	whole	D 17.2	D 9.8	1.76X	Penrose et al. (1975)

D = dry weight, W = wet weight, in ppm

fish and the crab Cancer anthonyi gave negative correlations. The best correlations were derived from using horse and cow hair, comparing areas downwind from a Cu smelter with controls. Two species of plants adapted to growing on mine waste had very high levels of As compared to controls. Aquatic plants growing in waters of a geothermal area had high concentrations in comparison with controls. Plants appear to be fairly effective for monitoring environmental gradients of As based on the few examples shown.

Beryllium

The only example known of biological measuring of environmental gradients of Be was using Spanish moss Tillandsia usnoides. Only three sites contained over 2 ppm ash weight out of 123 samples in the southeastern United States (Shacklette and Connor 1973).

Boron

No animal species are known to have been used for monitoring environmental gradients of boron.

Cabbage, Brassica olearaca capitata, grown in soil with 7 percent fly ash from Minnesota, had 145.0 ppm dry weight while the control had 21.0 ppm dry weight of boron, an increase of 6.9 X over the control (Furr et al. 1977).

Gladiola, Gladiolus grandiflorus unpotted indicator plants grown 45 m from a fiberglass plant had 342 ppm dry weight, while at 900 m the control had 20 ppm dry weight or an increase of 17.0 X over the control. Plants in a protected greenhouse growing in pots of contaminated soil had 410 ppm dry weight of B in terminal halves of leaves, showing much of the element came from soil instead of air pollution (Temple et al. 1978).

Spanish moss, Tillandsia usnoides growing in areas with agricultural and recreational use near highways with heavy traffic, urban sites with business and industrial uses had greater than average concentrations of boron. The highest levels had 300 ppm ash weight while the lowest levels had 70 ppm ash weight or an increase of 4.29 X. Spanish moss was used to locate geographic areas with low or high levels of boron (Shacklette and Connor 1973).

Three species of higher plants have been used successfully to measure environmental gradients of boron. No mosses, lichens or algae have been tested in available literature reviewed.

Cadmium

Forty-five species of plants and animals have been used to measure environmental gradients of cadmium pollution from various sources (Tables 13 and 14). The sources of Cd pollution include Zn, Pb and other non-ferrous smelters, Cd alloy plant, smelter-industrial area, Zn refinery, strip mine area, urban areas, trucking Pb concentrate, near highway, phosphate factory, Cu plant, highway, sewage outfalls, sludge fertilization, sludge dump, polluted harbors, estuaries and shore areas.

The animal species used for monitoring environmental gradients of Cd (Table 13) include seven species of mammals, ten species of molluscs, earthworms, one species of marine fish, and fruitflies. The plants used for measuring environmental gradients of Cd include 16 species of higher plants including food crops, grass, trees, and spanish moss. Six species of mosses and lichens and two species of marine algae were used as shown in Table 14.

The results show that various plant and animal species are quite effective in measuring environmental gradients of cadmium. A number of the species appear to be excellent candidates for biological monitoring.

Chromium

Twenty-one species of organisms have been used to measure environmental gradients of chromium. The sources of Cr pollution (Table 15) include cooling tower drift, sewage outfalls, ocean sewage dump, coal ash settling basins, industrial polluted bay, phosphate processing plant, gold smelter, serpentine areas, steelworks (using transplants of mosses and lichens), metallurgical industry, ferroalloy plant, general industry, and coal and oil combustion.

The organisms used for measuring Cr gradients include the cotton rat, one species of fish, two species of molluscs, three species of crustacea, one species of insect, seven species of higher plants and six species of mosses and lichens. All of the studies appear to be statistically valid except *Acartia clausi* which compares data from two authorities, and since the data are at low levels, taking into consideration the great difficulty in measuring low levels of Cr, these data are probably not statistically significant. The data from *Microstomus pacificus* are also very low and may not be significant.

Some animal species have been used effectively to monitor environmental gradients of chromium, however, plants appear to be more effective.

Cobalt

Environmental gradients of cobalt have been measured using two species of animals and eight species of higher plants. The sources of pollution included sludge amended soil, nuclear test fallout, a gold smelter, a nickel smelter, pollution from industry, and fossil fuel combustion.

The results of biological monitoring of environmental gradients of cobalt are shown in Table 16. Some of the data using higher plants such as *Beta*, *Betula*, *Comptonia* and *Vaccinium* were statistically significant by a small margin. The studies using the squid *Stenoteuthis* and the higher plants *Calamagrostis*, *Deschampsia*, *Rosa* and *Tillandsia* were more definitive. The spanish moss *Tillandsia* was very effective in comparing levels in different geographic areas. No mosses or lichens were found to have been used for monitoring of cobalt, in the literature reviewed.

Copper

Environmental gradients of copper have been monitored using 48 species of animals (Table 17) and plants (Table 18). No studies with vertebrate animals

TABLE 13. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF CADMIUM BY ANIMALS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Bos bovis	Pb smelter and trucking concentrate	hair	W 1.625	W 0.07	23.2X	Dorn et al. (1974)
Bos bovis	Pb smelter	kidney	W 3.7	W 1.4	2.6X	Dorn et al. (1973)
Bos bovis	Pb smelter	liver	W 0.9	W 0.24	3.8X	Dorn et al. (1973)
Bos bovis	Cd emission area-Germany	kidney	W 29.0	W 4.7	6.2X	Anke et al. (1976)
Equus caballus	smelter-Montana	mane	W 1.8	W 0.3	6.0X	Lewis (1972)
Oryctolagus cuniculus	Pb smelter-Montana	kidney	W 35.6	W 0.3	118.7X	Gordon (1972)
Ovis aries	smelter-Germany	kidney	W 26.0	W 2.1	12.4X	Anke et al. (1976)
Peromyscus leucopus	strip mine area	liver	W 0.55	W 0.12	4.6X	Curnow et al. (1977)
Sciurus carolinensis	urban versus rural	kidney	W 15.9	W 3.4	4.7X	Lynch (1973)
Spermophilus columbianus	Zn smelter	kidney	W 3.74	W 1.18	3.2X	Munshower (1972)
Spermophilus columbianus	Pb smelter	liver	W 1.4	W 0.02	70X	Gordon (1972)
FISH						
Belone belone	estuary vs. offshore	muscle	D 0.9	D 0.05	18X	Stevens and Brown (1974)

(continued)

TABLE 13. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MOLLUSCS						
Arcuatela demissus	heavy sewage sludge versus none	soft parts	D 7.13	D 1.98	3.6X	Valiela et al. (1974)
Buccinum undatum	dump area vs. Irish Sea	soft parts	D 5.75	D 2.2	2.6X	Mackay et al. (1972)
Crassostrea gigas	sewage polluted versus non-polluted	soft parts	W 15.5	W 0.9	16.7X	Ayling (1973)
Crassostrea gigas	contam. estuary versus non-contam.	soft parts	W 20.9	W 3.5	6.0X	Thrower and Eustace (1973)
Crassostrea gigas	harbor contam. versus non-contam.	soft parts	D 20.1	D 1.87	10.7X	Darracott and Watling (1975)
Helix aspersa	smelter-terrestrial vs. uncontam.	soft parts	D 64.71	D 6.04	10.7X	Coughtrey and Martin (1976)
Helix aspersa	smelter-terrestrial vs. uncontam.	digestive gland	D 198.5	D 14.9	13.3X	Coughtrey and Martin (1976)
Littorina littoralis	near metal smelter vs. unpolluted	soft parts	D 20.0	D 6.3	3.2X	Steinner and Nickless (1974a)
Mytilus edulis	near metal smelter vs. unpolluted	soft parts	D 140.0	D 15.5	9.0X	Steinner and Nickless (1974a)

(continued)

TABLE 13. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Nucella lapillus	polluted Bristol Channel versus low pollution	soft parts	D 780.0	D 36.0	21.7X	Steinner and Nickless (1974b)
Ostrea angasi	polluted estuary versus clean	soft parts	W 18.7	W 2.3	8.1X	Thrower and Eustace (1973)
Patella sp.	polluted Bristol Channel versus low pollution	soft parts	D 220.0	D 11.0	20X	Steinner and Nickless (1974b)
Patella vulgata	polluted area versus non-polluted	soft parts	W 62.3	W 2.0	31.1X	Peden et al. (1973)
INSECTA						
Drosophila sp.	near smelter vs. distant, Missouri	whole	D 8.1	D 2.6	3.1X	Lower (1974)
ANNELIDA						
Allolobophora spp. and Lumbricus sp.	near highway vs. control	whole	D 12.6	D 3.0	4.2X	Gish and Christensen (1973)

D = dry weight, W = wet weight, in ppm

TABLE 14. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF CADMIUM BY PLANTS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Allium cepa	smelter area-Germany	bulb	W 0.40	W 0.08	5X	Anke et al. (1976)
Allium fistulosa	refinery Japan	bulb & stem	W 14.0	W 1.0	14X	Kobayashi (1972)
Artemisia tridentata	PO_4 factory Idaho	top	D 104	D 30.5	3.4X	Gough & Severson (1976)
Avena sativa	Cd alloy plant, Sweden	top	W 0.095	0.026	3.6X	Kjellstrom et al. (1974)
Brassica rapa	smelter area-Germany	leaf	W 5.87	W 0.19	30.9X	Anke et al. (1976)
Clintonia borealis	smelter, 1.9 km vs. 11 km		D 15.7	D 0.4	39.3X	LeBlanc et al. (1974)
Festuca rubra	downwind from industry 1.5 versus 16 km	top	D 40.0	D 1.4	28.6X	Goodman & Roberts (1971)
Juniperus virginianus	near Pb smelter ore trucks	branch	A 9.3	A 2.8	3.3X	Connor et al. (1971)
Lactuca sativa	smelter town versus non-	leaf	D 10.6	D 1.0	10.6X	Gordon (1972)
Lycopersicum esculentum	smelter area-Germany	fruit	D 0.18	D 0.03	6.0X	Anke et al. (1974)

(continued)

TABLE 14. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Morus sp.	dist. from refinery 0.4 km vs. control	leaf	D 17.0	D 1.0	17X	Kobayashi (1972)
Picea mariana	dist. from smelter 1.1 versus 11 km	leaf	D 2.3	D 0.4	5.8X	LeBlanc et al. (1974)
Tillandsia usnoides	industry and combustion	whole	D 1.0	D 0.1	10X	Shacklette (1972)
Triticum aestivum	4 km from Cu plant vs. control	grain	W 0.095	D 0.041	2.3X	Kjellstrom et al. (1975)
Ulmus glabra	near smelter vs. 10-15 km away	unwashed leaf	D 50.0	D 0.25	200X	Little and Martin (1972)
Zea mays	polluted versus non-polluted	grain	D 2.0	D 0.1	20X	Shacklette (1972)
MOSSES						
Eurynchium sp.	dist. from Zn smelter "near" to 2.9 km vs. 6 km	plant	D 148.0	D 49.0	3X	Burkitt et al. (1972)
Hylocomium splendens	urban area vs. 100 km away	plant	3.5	1.0	3.5X	Jaakkola et al. (1971)
Hypnum compressifolium	smelter industrial area, 8.0 vs. 25 km	plant	D 7.0	D 2.0	3.5X	Goodman and Roberts (1971)

(continued)

TABLE 14. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
LICHENS						
Cladonia alpestris	Zn refinery near versus control	plant	D 1.0	D 0.15	6.7X	Jaakkola et al. (1971)
Lasellia populosa	Zn smelter area versus control	plant	D 32.0	D 1.0	32X	Nash (1975)
Parmelia sp.	Zn smelter area 1-3 versus 6 mi	plant	D 81.0	D 20.0	4X	Burkitt et al. (1972)
ALGAE						
Fucus serratus	polluted estuary vs. control	plant	D 53.0	D 0.3	176X	Leatherland and Burton (1974)
Fucus vesiculosus	polluted Bristol Channel vs. Irish Sea	plant	D 13.8	D 2.2	6.3X	Fuge and James (1974)

D = dry weight, W = wet weight, in ppm

have been successful. Although there is significant bioaccumulation, there is biominification in higher trophic level predators, perhaps due to regulatory mechanisms preventing high accumulation in vertebrate animals.

The sources of copper include: Pb smelters, Hg mines, Cu mine drainage, Cu mine and smelter, sewage outfall, industrial effluent, steam electric plant effluent, ocean disposal dump sites, desalination plant effluent, coal ash effluent, Cu mine slag heap, Cu Ni smelters, sewage sludge, contaminated bay, steelworks, metal smelters, and metallurgic industry. Some additional studies compared various polluted areas but without using a control or nearby baseline.

Mammals, amphibia and fish (Table 17) were used for monitoring environmental gradients of Cu but the results were not significant, and in some cases negative. However, molluscs and especially filter feeding

TABLE 15. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF CHROMIUM

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Sigmodon hispidus	cooling tower drift	hair	W 4.397	W 0.395	11.1X	Taylor et al. (1975)
Sigmodon hispidus	cooling tower drift	pelt	W 1.056	W 0.092	11.5X	Taylor et al. (1975)
FISH						
Microstomus pacificus	sewage outfall	gonad and liver	D 0.4	D <0.2	2.0X	McDermott et al. (1976)
MOLLUSCS						
Buccinum undatum	ocean sewage dump	soft parts	D 25.0	D 0.2	12.5X	Mackay et al. (1972)
Patella vulgata	sewage outfall	soft parts	D 20.85	D 12.3	1.7X	Navrot et al. (1974)
ARTHROPODS						
"Crab"	domestic and industrial waste	shell	D 8.0	D 2.5	3.2X	Hung et al. (1975)
Acartia clausi	industrial polluted bay	whole	D 3.26	D 1.5	2.2X	Fukai and Broquet (1965)
Crangon allmani	ocean sewage dump	soft parts	D 13.0	D 9.0	1.4X	Mackay et al. (1972)
Chironomidae	coal ash basin	whole	88.0	20.0	4.4X	Cherry et al. (1979)

(continued)

TABLE 15. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
HIGHER PLANTS						
Artemisia tridentata	phosphate process plant	leaf, stem & flowers	A 500.0	A 30.0	16.7X	Gough and Severson (1976)
Calamagrostis canadensis	gold smelter	leaf & stem	D 21.9	D 2.53	8.7X	O'Toole et al. (1971)
Cassinia vauvilliersii	serpentine	leaf	A 1,057.5	A 21.5	49.2X	Lyon et al. (1971)
Plantago maritima	serpentine	leaf	A 91.0	A 5.0	18.2X	Shewry and Peterson (1976)
Silene maritima	serpentine	leaf	A 74.0	A 9.0	8.2X	Shewry and Peterson (1976)
Thymus drucei	serpentine	leaf	A 130.0	A 32.0	4.1X	Shewry and Peterson (1976)
Tillandsia usnoides	industry and fuel	whole	A 1,500.0	A 7.0	214.3X	Shacklette and Connor (1973)
MOSSES AND LICHENS						
Dicranoweisia cirrata	steelworks (transplants)	whole	D 62.2	D 3.9	16.0X	Pilegaard (1979)
Hylocomium splendens	metallurgy industry	whole	D 6.0	D 1.5	4.0X	Ruhling and Tyler (1973)
Hypogymnia physodes	steelworks (transplants)	whole	D 47.2	D 4.3	11.0X	Pilegaard (1979)
Hypnum cupressiforme	Ferro-alloy	whole	D 10,000	D 9.0	1,111.1X	Tyler (1971)

(continued)

TABLE 15. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Hypnum cupressiforme	industry and fuel	whole	D 7.7 (1969)	D 5.8 (1970)	1.3X	Ruhling and Tyler (1969)
Lecanora conizaeoides	steelworks	whole	D 121.0	D 3.8	31.8X	Pilegaard (1978)
Peltigera rufescens	steel smelter	whole	127.4	25.81	4.9X	Seaward (1973)

D = dry weight, W = wet weight, A = ash weight, in ppm

bivalves have been used successfully. In addition 17 species of crustacea and echinoderms have been used most of which were effective in monitoring gradients of Cu.

Plants have been used for monitoring environmental gradients of Cu and 16 species of higher plants, four species of mosses, three species of lichens, and four species of marine algae have been used successfully (Table 18). In summary, certain molluscs and both higher and lower plants appear to be suitable organisms for monitoring environmental gradients of Cu.

Lead

Over 95 species of animals (Table 19) and plants (Table 20) have been used to successfully monitor environmental gradients of lead. The sources of lead include tetraethyl lead from vehicles on heavy traffic highways and in urban areas, gasoline station areas, abandoned Pb Zn mines, Pb smelter and trucking Pb concentrate, Pb piping of water supply, Pb arsenate residue in old orchards, urban versus rural, ingestion of Pb fishing weights, worms from contaminated soil, Pb tailings pond, spoil pond, contaminated estuary, sewer outfall, sewage sludge oceanic deposit dump, city port, dredging spoil disposal, polluted bay, Pb geological anomaly, industrial complex, Zn refinery, mine runoff, contaminated marsh, steelworks, regional industry, Cu smelter, and steel smelter.

A very large number of studies have been carried out measuring gradients of lead from heavily travelled roads and highways. Many of these were not included to prevent repetition. Also a number of studies without comparative data on levels of Pb in the environment were omitted. Many of these were comparisons of polluted or semipolluted sites without a measured true gradient.

TABLE 16. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF COBALT BY PLANTS AND ANIMALS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Cavia porcellus	sludge-amended soil	adrenal	D 1.8	D 0.5	3.6X	Furr et al. (1976)
MOLLUSCA						
Stenoteuthis bartrami	nuclear test fallout	liver	W 2,033 pCi/kg Co^{60}	W 0.0	2,033X	Folsom and Young (1965)
HIGHER PLANTS						
Beta vulgaris cicla	sludge-amended soil	leaf	D 2.3	D 1.6	1.4X	Furr et al. (1976)
Calamagrostis canadensis	gold smelter	leaf	D 5.78	D 1.61	3.6X	O'Toole et al. (1971)
Betula papyrifera	Ni smelter	leaf	D 10.0	D 6.5	1.5X	Hutchinson and Whitby (1974)
Comptonia peregrina	Ni smelter	leaf	D 10.0	D 7.0	1.4X	Hutchinson and Whitby (1974)
Deschampsia flexuosa	Ni smelter	leaf	D 32.5	D 5.5	5.9X	Hutchinson and Whitby (1974)
Rosa acicularis	gold smelter	fruit & leaf	D 1.14	D 0.06	19.0X	O'Toole et al. (1971)
Tillandsia usnoides	industry and fuel combustion	whole	A 70.0	A 7.0	10.0X	Shacklette and Connor (1973)
Vaccinium angustifolium	Ni smelter	leaf	D 10.0	D 5.5	1.8X	Hutchinson and Whitby (1974)

D = dry weight, W = wet weight, A = ash weight, in ppm

TABLE 17. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF COPPER IN ANIMALS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Bos bovis	Pb smelter	hair	D 8.26	D 7.25	N.S.	Dorn et al. (1974)
AMPHIBIA						
Rana temporaria	Hg mine	liver	W 318.9	D 176.4	1.8X	Byrne et al. (1975)
FISH						
Microstomus pacificus	sewage outfall	liver	D 9.5	D 7.4	N.S.	McDermott et al. (1976)
Paralabrax clathratus	steam plant effluent	liver	D 5.0	D 6.0	-N.S.	Stapleton (1968)
Paralabrax clathratus	steam plant effluent	muscle	D 3.5	D 2.0	N.S.	Stapleton (1968)
MOLLUSCS						
Busycon canaliculatum	ocean disposal site	digestive gland	W 1,135.0	W 32.4	35.0X	Grieg et al. (1977)
Crassostrea gigas	urban and industry polluted bay	soft parts	W 132.4	W 46.9	2.8X	Thrower and Eustace (1973)
Crassostrea glomerata	Cu mine drainage	soft parts	W 380.0	W 165.0	2.3X	Nielsen and Nathan (1975)
Crassostrea virginica	steam plant, urban and industry	soft parts	240.0	5.0	48.0X	Bender et al. (1972)
Crassostrea virginica	steam plant effluent	soft parts	D 850	D 400	2.1X	Roosenburg (1969)

(continued)

TABLE 17. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Helix aspersa	smelter	whole	D 67.93	D 39.4	1.7X	Coughtrey and Martin (1976)
Mytilus californianus	urban sewage outfall	digestive gland	D 69.0	D 14.0	4.9X	Alexander and Young (1976)
Mytilus edulis	Cu mining and smelting	soft parts	D 130.0	D 15.0	8.7X	Stenner and Nickless (1974a)
Mytilus gallo-provincialis	urban sewage	soft parts	D 53.9	D 6.1	8.8X	Fowler and Oregione (1976)
Nucella lapillus	industrial waste	soft parts	D 822.5	D 70.0	11.8X	Stenner and Nickless (1974b)
Patella vulgata	industrial waste	soft parts	D 12.0	D 2.0	6.0X	Peden et al. (1973)
Patella vulgata	urban sewage outfall	soft parts	D 10.5	D 6.6	1.6X	Navrot et al. (1974)
Patella vulgata	desalination plant effluent	soft parts	D 89.9	D 4.86	18.5X	Romeril (1977)
Placopecten magellanicus	ocean disposal site	soft parts	D 11.17	D 4.44	2.5X	Pesch et al. (1977)
CRUSTACEA						
Cancer magister	urban sewer outfall	soft parts	D 94.0	D 35.0	2.7X	Parsons et al. (1973)
Cragon allmani	sewage dump site	soft parts	D 203.0	D 117.0	1.7X	Mackay et al. (1972)

(continued)

TABLE 17. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
"Crayfish"	coal ash effluent		41.9	14.62	2.9X	Cherry et al. (1979)
Pandalus montagui	sewage dump site	soft parts	D 88.0	D 70.0	N.S.	Mackay et al. (1972)
Tracheoniscus rathkei	Cu mine slag heap	whole	D 538.0	D 74.0	7.3X	Wieser et al. (1976)
ECHINODERMS						
Arbacia lixula	urban sewage	soft parts	D 16.6	D 7.0	2.4X	Sheppard and Bellamy (1974)

D = dry weight, W = wet weight, in ppm

The 45 studies using animals (Table 19) and the 50 studies using plants (Table 20) for measuring environmental gradients of Pb show that a large number of species accumulate lead levels that can be correlated with levels of Pb in the environment. In addition, there are many other species which could be included. This allows the selection of a large number of potential biological monitoring organisms.

Mercury

Mercury is fairly widespread but is also naturally concentrated in mercuriferous areas. Man has caused pollution concentrations in many different types of areas and there have been over 42 studies using animals but only seven using plants for monitoring environmental gradients of mercury (Table 21). The types of sources of mercury in these studies include chlorakali and chlorine plants, Hg mines, Hg distillation plant, Hg slimicides from pulp paper factory, effluent Hg from gold mining, cinnabar refinery, municipal wastewater, sewage discharge, industry, coal fly ash disposal basin, gold smelter, exposure to fly ash near stacks and urban and industrial pollution.

Mammals, birds and amphibia have been used successfully to monitor Hg using liver tissue, hair, and kidney of mammals and feathers of birds. Twelve species of fish have been used, especially predators for monitoring. Molluscs, crustacea, insects and annelid worms accumulate Hg and have been used in monitoring environmental gradients of Hg.

TABLE 18. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF COPPER IN PLANTS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
HIGHER PLANTS						
Acer rubrum	Cu Ni smelters	leaf	D 37.0	D 16.0	2.3X	Hutchinson and Whitby (1974)
Anacharis canadensis	Cu Ni smelters	whole	W 510.0	D 18.0	28.3X	Hutchinson et al. (1975)
Beta vulgaris cicla	sewage sludge	leaf & stem	D 97.0	D 4.6	21.1X	Furr et al. (1976)
Betula papyrifera	Cu Ni smelters	leaf	D 94.5	D 14.0	6.8X	Hutchinson and Whitby (1974)
Comptonia peregrina	Cu Ni smelters	leaf & stem	D 57.3	D 14.3	4.0X	Hutchinson and Whitby (1974)
Deschampsia flexuosa	Cu Ni smelters	leaf & stem	D 726.0	D 13.0	55.9X	Hutchinson and Whitby (1974)
Equisetum fluviatile	mine effluent	stem	D 33.0	D 13.0	2.5X	Ray & White (1976)
Festuca rubra	smelter	leaf & stem	D 15.0	D 5.0	3.0X	Goodman and Roberts (1971)
Nuphar variegatum	Cu Ni smelters	leaf	W 18.0	W 4.0	4.5X	Hutchinson et al. (1975)
Panicum virgatum	Pb smelter	leaf & stem	D 327.0	D 25.3	12.9X	Lagerwerff et al. (1972)
Pinus banksiana	Cu Ni smelters	leaf & stem	D 43.2	D 10.7	4.0X	Hutchinson and Whitby (1974)

(continued)

TABLE 18. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Populus grandidentata	Cu Ni smelters	leaf & stem	D 75.0	D 11.6	6.5X	Hutchinson and Whitby (1974)
Potamogeton richardsoni	mine effluent	leaf & stem	D 171.0	D 2.8	61.1X	Ray & White (1976)
Tillandsia usnoides	urban and industrial air pollution	whole	A 2,000	A 20	100.0X	Shacklette and Connor (1973)
Vaccinium angustifolium	Cu Ni smelters	leaf & stem	D 49.6	D 11.2	4.4X	Hutchinson and Whitby (1974)
Zostera sp.	contaminated bay	leaf	D 1,350.	D 22.5	60.0X	Stenner and Nickless (1975)
MOSSES						
Dicranoweisia cirrata	steelworks	whole	D 237.0	D 10.3	23.0X	Pilegaard (1979)
Hylocomium splendens	metallurgic industry	whole	D 12.0	D 5.0	2.4X	Ruhling and Tyler (1973)
Hylocomium splendens	copper mine area	whole	D 724.0	D 346.0	2.1X	LeBlanc et al. (1974)
Hypnum compressiforme	smelter	whole	D 65.0	D 11.0	5.9X	Goodman and Roberts (1971)
Pleurozium schreberi	copper mine area	whole	D 752.5	D 236.5	3.2X	LeBlanc et al. (1974)
LICHENS						
Hypogymnia physodes	steelworks	whole	D 172.3	D 8.3	20.8X	Pilegaard (1979)

(continued)

TABLE 18. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Lecanora conizaeoides	steelworks	whole	D 277.0	D 7.9	35.1X	Pilegaard (1978)
Peltigera rufescens	steelworks	whole	91.35	16.14	5.7X	Seaward (1973)
ALGAE						
Ascophyllum nodosum	metal smelters	whole	D 170.0	D 32.5	5.2X	Haug et al. (1974)
Ascophyllum nodosum	metal smelters	whole	D 85.0	D 4.0	21.3X	Stenner and Nickless (1974a)
Enteromorpha sp.	metal smelters	whole	D 110.0	D 24.0	4.6X	Stenner and Nickless (1974a)
Fucus spiralis	desalination plant effluent	whole	D 86.1	D 2.0	43.1X	Romeril (1977)
Fucus vesiculosus	metal smelters	whole	D 118.0	D 10.0	11.8X	Stenner and Nickless (1974a)

D = dry weight, W = wet weight, in ppm

Higher plants generally do not accumulate and retain mercury, but there are a few mercuriferous plants including Holostium which have been used for biogeochemical prospecting for Hg. Only three species of higher plants have been used successfully for measuring environmental gradients of Hg. Three species of moss, one fungal species, but no species of lichens are known to have been used for monitoring environmental gradients of Hg.

Nickel

There is an abundance of data on the levels of nickel in many groups of organisms, but in animals the data are rather variable. There are ten examples of animals being used for measuring environmental gradients of Ni and some of the results are not statistically significant (Table 22). No mammals or birds have been used. One species of marine fish, the dover sole, was used and liver tissue showed poor correlation with Ni in sewage outfall. The

TABLE 19. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF LEAD BY ANIMALS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Apodemus sylvaticus	abandoned Pb Zn mines	bone	D 270.5	D 16.3	16.6X	Roberts et al. (1978)
Blarina brevicauda	highway traffic	whole	D 17.2	D 3.3	5.2X	Getz et al. (1977)
Blarina brevicauda	highway traffic	whole	D 14.0	D 4.0	3.5X	Quarles et al. (1974)
Blarina brevicauda	highway traffic	whole	W 26.2	W 1.85	14.2X	Dorn et al. (1974)
Bos bovis	Pb smelter & trucking concentrate	hair	D 94.1	D 2.2	42.8X	Clark (1979)
Bos bovis	Pb piping	blood	W 0.66	W 0.15	4.4X	Ward et al. (1977)
Bos bovis	Pb smelter	milk	W 0.14	W 0.034	4.1X	Lagerwerff and Brower (1974)
Canis familiaris	gasoline station area	blood	W 6.91	W 0.27	25.6X	Ward et al. (1977)
Clethrionomys glariolus	abandoned Pb Zn mine	whole	D 18.5	D 2.5	7.4X	Roberts et al. (1978)
Cryptotis parva	highway traffic	whole	D 12.3	D 7.4	1.7X	Getz et al. (1977)
Equus caballus	smelter	kidney	W 40.4	W 3.1	13.0X	Goodman and Roberts (1971)
Equus caballus	smelter	mane	D 35.0	D 7.1	4.9X	Lewis (1972)

(continued)

TABLE 19. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Eutamias townsendii	highway traffic	hair	D 235.6	D 6.0	39.3X	Raymond and Forbes (1975)
Microtus agrestis	abandoned Pb Zn mine	whole	D 140.4	D 8.56	16.4X	Roberts and Johnson (1978)
Microtus ochrogaster	highway traffic	whole	D 8.1	D 3.3	2.5X	Getz et al. (1977)
Microtus pennsylvanicus	Pb arsenate residue	kidney	D 31.0	D 2.95	10.5X	Elfving et al. (1978)
Peromyscus maniculatus	highway traffic	whole	D 5.5	D 2.8	1.97X	Getz et al. (1977)
Rattus norvegicus	urban versus rural	bone	W 200.0	W 10.3	19.4X	Mouw et al. (1975)
Reithrodontomys megalotis	highway traffic	whole	D 10.8	D 3.1	3.5X	Getz et al. (1977)
Sorex araneus	abandoned Pb Zn mine	whole	D 11.2	D 0.88	12.7X	Roberts et al. (1978)
BIRDS						
Columba livia	urban versus rural	femur	W 31.6	W 2.0	15.8X	Ohi et al. (1974)
Cygnus olor	ingested Pb fishing weights	bone	D 762.0	D 32.0	23.8	Simpson et al. (1979)
Falco tinnunculus	urban versus rural	egg-shell	D 2.80	D 1.52	1.84X	Grandjean (1976)
Passer domesticus	urban versus rural	femur	D 130.4	D 16.9	7.7X	Getz et al. (1977a)
Quiscalus quiscala	urban versus rural	femur	D 62.8	D 21.5	2.9X	Getz et al. (1977a)

(continued)

TABLE 19. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Sturnus vulgaris	urban versus rural	femur	D 213.0	D 12.8	16.6X	Getz et al. (1977a)
Sturnus vulgaris	urban versus rural	body without skin, beak, feet, and wing	W 1.088	W 0.681	1.6X	White et al. (1977)
Turdus migratorius	urban versus rural	femur	D 133.7	D 41.3	3.2X	Getz et al. (1977a)
AMPHIBIA						
Xenopus laevis	worms from contaminated soil	bone	W 23.97	W 5.0	4.8X	Ireland (1977)
Rana sp.	Pb tailings pond	tadpole	D 4,139.0	D 37.0	111.9X	Gale et al. (1976)
FISH						
Platichthys flesus	contaminated estuary	whole	D 28.2	D 19.1	1.5X	Hardisty et al. (1974)
Fundulus heteroclitus	spoil pond	whole	4.5	0.9	5.0X	Drifmeyer & Odum (1975)
Ictalurus sp.	Pb tailings pond	gill	D 41.0	D 15.0	2.7X	Gale et al. (1976)
Lepomis macrochirus	Pb tailings pond	whole	D 128.0	D 14.0	9.1X	Gale et al. (1976)
Micropterus sp.	Pb tailings pond	gill	D 41.0	D 15.0	5.0X	Gale et al. (1976)
MOLLUSCS						
Buccinum undatum	sewage dump	soft parts	D 41.0	D 5.4	7.6X	Mackay et al. (1972)

(continued)

TABLE 19. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Helix aspersa	smelter	soft parts	D 28.6	D 18.8	1.5X	Coughtrey and Martin (1976)
Mytilus californianus	sewer outfall	soft parts	D 23.4	D <2.2	10.6X	Graham (1972)
Mytilus edulis	metal smelter	soft parts	D 3,100.0	D 16.0	193.7X	Stenner and Nickless (1974a)
Mytilus gallo-provincialis	city port	soft parts	D 66.6	D 10.7	6.2X	Fowler and Oregione (1976)
CRUSTACEA						
Cambarus sp.	Pb tailings pond	whole	D 500.0	D 6.0	83.3X	Gale et al. (1976)
Cragon allmani	sewage sludge dump	soft parts	D 32.0	D 17.0	1.9X	Mackay et al. (1972)
Palaemonetes pugio	spoil disposal	whole	11.0	0.2	55.0X	Drifmeyer & Odum (1975)
Pandalus montagui	sewage sludge dump	soft parts	D 31.0	D 24.0	1.3X	Mackay et al. (1972)
ECHINODERMS						
Arbacia lixula	polluted bay	soft parts	D 58.6	D 21.0	2.8X	Sheppard and Bellamy (1974)
Paracentrotus lividus	polluted bay	soft parts	D 42.3	D 20.0	2.1X	Sheppard and Bellamy (1974)

(continued)

TABLE 19. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
ANNELID WORMS						
Allolobophora 3 spp. and *Lumbricus terrestris*	highway traffic	whole	D 269.8	D 52.7	5.1X	Gish and Christensen (1973)
Eisenia rosea	sewage sludge	whole	D 142.0	D 32.0	4.4X	Illinois (1972)
Lumbricus terrestris	derelict Pb Zn mine	whole	D 146.0	D 4.0	36.5X	Roberts and Johnson (1978)

D = dry weight, W = wet weight, in ppm

freshwater white sucker and northern pike had high levels of nickel in muscle in a Ni smelter area in Ontario. These data were compared with levels in muscles in other areas, which is not necessarily valid since measurements were made by several investigators.

Three species of molluscs and three species of crustacea showed good correlation with environmental gradients of Ni. While data on use of an echinoderm and annelid worms are presented in Table 22 the data for *Arbacia* are statistically not significant, and for annelids the data approach significance.

Higher plants are excellent bioaccumulators of Ni and have been used extensively to measure environmental gradients. Results from using 19 species are shown in Table 23, measuring gradients around a nickel smelter, a phosphate processing plant, industrial areas, highways and a serpentine area. Environmental gradients of nickel monitored by the plants correlated with levels measured directly in the environment. Many species of plants are hyperaccumulators or bioconcentrators and store large quantities of Ni. Many species are therefore excellent bioindicators of nickel metal deposits and ores. This is due to plants having nearly unregulated accumulation of Ni while most animals have limited absorption and high excretion rates, or in some cases regulatory capability.

Four species of mosses and five species of lichens have been used to measure environmental gradients of Ni around steelworks, steel smelter, Ni smelter, and industry. Two studies have used mosses to measure the change in levels of nickel over a period of time comparing museum collections with

TABLE 20. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF LEAD BY PLANTS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Acer pseudoplatanus	highway	washed leaf	A 840.0	A 20.0	42.0X	Ward et al. (1974)
Albizia zugia	Pb anomaly	leaf	D 23.0	D 0.4	57.5X	Hawkes and Webb (1962)
Allium cepa	highway		W 8.0	W 4.0	2.0X	Mollenhauer (1972)
Avena sativa	highway		W 6.4	W 3.4	1.9X	Mollenhauer (1972)
Baphia nitida	Pb anomaly	leaf	D 16.0	D 0.4	40.0X	Hawkes and Webb (1962)
Beta vulgaris cicla	highway	leaf	D 238.0	D 154.0	1.5X	Impens et al. (1973)
Beta vulgaris cicla	sewage sludge	leaf & stem	D 6.8	D 2.5	2.7X	Furr et al. (1976)
Brassica parachinensis	highway	unwashed leaf	D 84.0	D 46.0	1.8X	Wong & Tam (1978)
Daucus carota	old orchard soil	root	D 7.1	D 1.0	7.1X	Elfving et al. (1978)
Festuca rubra	industry	leaf	D 814.0	D 14.5	56.1X	Goodman and Roberts (1971)
Fraxinus excelsior	highway	washed leaf	A 460.0	A 50.0	9.2X	Ward et al. (1974)
Glycine max	highway	pod	D 15.9	D 5.3	3.0X	Ter Haar (1970)
Glycine max	highway	---	D 35.0	D 8.0	4.4X	Illinois (1971)
"Grass"	Pb smelter	leaf & stem	D 2,714.0	D 445.0	6.1X	DeKoning (1974)

(continued)

TABLE 20. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Lactuca sativa	highway		W 44.2	W 4.5	9.8X	Mollenhauer (1972)
Morus sp.	Zn refinery	leaf	D 110.0	D 60.0	1.8X	Kobayashi (1972)
Parkia oliveri	Pb anomaly	leaf	D 13.0	D 0.4	32.5X	Hawkes and Webb (1962)
Phragmites communis	dredge spoil		D 4.4	D 0.5	8.8X	Drifmeyer & Odum (1975)
Pinus echinata	Pb smelter	needle	D 3,546.4	D 123.3	28.8X	Bolter et al. (1973)
Pinus strobus	highway	twig and needle	D 160.0	D 50.0	3.2X	Smith (1971)
Platanus orientalis	highway	washed leaf	A 1,020.0	A 80.0	17.8X	Ward et al. (1974)
Potamogeton richardsoni	mine runoff	root	12.5	3.66	3.4X	Ray & White (1976)
Potamogeton sp.	Pb tailings pond		D 11,300	D 100.0	113.0X	Jennett and Wixson (1975)
Quercus alba	Pb smelter	leaf	D 574.3	D 54.5	10.5X	Hemphill and Pierce (1975)
Quercus robur	highway	washed leaf	A 580.0	A 100.0	5.8X	Ward et al. (1974)
Quercus stellata	Pb smelter	leaf	D 3,776.7	D 169.0	22.3X	Bolter et al. (1973)
Robinia pseudoacacia	highway	leaf	A 234.7	D 53.5	4.4X	Majerus and Denaeyer (1973)

(continued)

TABLE 20. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Spartina alternifolia	dredge spoil		D 5.1	D 1.9	2.7X	Drifmeyer & Odum (1975)
Spartina alternifolia	contaminated marsh		D 23.2	D 5.4	4.3X	Banus et al. (1974)
Spartina patens	dredge spoil		D 9.1	D 0.8	11.4X	Drifmeyer & Odum (1975)
Triticum aestivum	highway	husk	D 17.8	D 6.2	2.9X	Ter Haar (1970)
Ulmus campestris	smelter	unwashed leaf	D 18,500	D 20.0	925.0X	Little (1973)
Ulmus procera	highway	washed leaf	A 680.0	A 60.0	11.3X	Ward et al. (1974)
Vaccinium pallidum	Pb smelter	leaf	D 495.3	D 41.6	11.9X	Hemphill and Pierce (1974)
Vitex cuneata	Pb anomaly	leaf	D 6.0	D 0.6	10.0X	Hawkes and Webb (1962)
Zea mays	highway	husk	D 12.6	D 5.7	2.2X	Ter Haar (1970)
Zea mays	sludge-amended soil	root	D 542.0	D 114.0	4.8X	Kirkham (1975)
MOSSES						
Dicranoweisia cirrata	steel-works	whole transplanted	D 827.0	D 96.0	8.6X	Pilegaard (1979)
Hyocomium splendens	industry, regional	whole	D 110.0	D 7.0	15.7X	Ruhling and Tyler (1973)
Hylocomium splendens	Cu smelter	whole	D 17,320	D 196.5	88.1X	LeBlanc et al. (1974)

(continued)

TABLE 20. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Hypnum cupressiforme	urban industry	whole	D 430.0	D 100.0	4.3X	Goodman and Roberts (1971)
Hypnum cupressiforme	urban industry	trans-plants	D 4,675	D 197.0	23.7X	Goodman and Roberts (1971)
Pleurozium schreberi	Cu smelter	whole	D 695.0	D 62.5	11.1X	LeBlanc et al. (1974)
LICHENS						
Hypogymnia physodes	steel-works	whole, trans-planted	D 1,018	D 75.0	13.6X	Pilegaard (1979)
Lecanora conizaeoides	steel-works	whole	D 1,930	D 31.0	62.3X	Pilegaard (1978)
Peltigera rufescens	steel smelters	whole	454.4	78.7	5.8X	Seaward (1973)
ALGAE						
Ascophyllum nodosum	metal smelter	whole	D 62.0	D 0.7	88.6X	Stenner and Nickless (1974a)
"Algal blooms"	Zn smelter waste	whole	W 5,750	W 150.0	38.3X	Trollope and Evans (1976)
Cladophora sp.	Pb tailings pond	whole	D 11,300	D 200	56.5X	Jennett and Wixson (1975)
Fucus vesiculosus	metal smelter	whole	D 202.0	D 10.0	20.2X	Stenner and Nickless (1974a)

D = dry weight, W = wet weight, in ppm

TABLE 21. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF MERCURY

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Apodemus sylvaticus	chloralkali plant	hair	W 0.78	W 0.12	6.5X	Bull et al. (1977)
Clethrionomys glareolus	chloralkali plant	hair	W 0.91	W 0.18	5.1X	Bull et al. (1977)
Felis domesticus	chloralkali plant	liver	W 91.3	W 3.6	25.4X	Takeuchi et al. (1962)
Oryctolagus cuniculus	Hg mine and distillation plant	kidney	W 44.5	W 0.01	4,450.0X	Byrne et al. (1971)
Phoca hispida saimensis	slimicides paper factory	hair	W 57.0	W 5.0	11.4X	Häsänen (1974)
BIRDS						
Actitis macularia	effluent Hg from gold mining	liver	W 0.38	W 0.12	3.17X	Hesse et al. (1975)
Falco peregrinus	1834-1941 versus 1943-1965	feather	W 49.0	W 2.5	19.6X	Berg et al. (1966)
Haliaetus albicilla	1832-1949 versus 1952-1965	tail feather	W 57.1	W 6.6	8.7X	Berg et al. (1966)
Hirundo rustica	effluent Hg from gold mining	liver	W 0.36	W 0.06	6.0X	Hesse et al. (1975)
Larüs delawärensis	effluent Hg from gold mining	liver	W 0.89	W 0.22	4.1X	Hesse et al. (1975)

(continued)

TABLE 21. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Petrochelidon pyrrhonota	effluent Hg from gold mining	liver	W 0.18	W 0.06	3.0X	Hesse et al. (1975)
Sterna albifrons	effleuent Hg from gold mining	liver	W 1.53	W 0.44	4.1X	Hesse et al. (1975)
AMPHIBIA						
Bufo bufo	Hg mine	liver	W 23.9	W 0.9	26.6X	Byrne et al. (1975)
Rana temporaria	Hg mine	liver	W 25.9	W 0.48	54.0X	Byrne et al. (1975)
FISH						
Ambloplites rupestris	chloralkali plant	muscle	W 6.22	W 0.55	11.3X	Fimreite and Reynolds (1973)
Catostomus commersoni	chloralkali plant	muscle	W 3.13	W 1.00	3.1X	Fimreite and Reynolds (1973)
Esox lucius	chloralkali plant	muscle	W 15.17	W 5.25	2.9X	Fimreite and Reynolds (1973)
Esox lucius	paper factory	muscle	W 3.3	W 0.55	6.0X	Westoo (1969)
Esox lucius	chloralkali plant	muscle	W 4.8	W 0.24	20.0X	Sumner et al. (1972)
Leuciscus hakuensis	polluted river	muscle	D 15.0	D 1.5	10.0X	Matida and Kumada (1969)
Lota lota	chloralkali plant	muscle	W 17.6	W 0.09	195.6X	Takeuchi et al. (1977)

(continued)

TABLE 21. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Parophrys vetulus	chloralkali plant	muscle	W 0.171	W 0.015	11.4X	Buhler et al. (1973)
Perca flavescens	chloralkali plant	muscle	W 0.65	W 0.20	3.3X	Fimreite et al. (1971)
Perca fluviatilus	wood pulp factory	muscle	W 4.93	W 0.34	14.5X	Underdal and Hastein (1971)
Psettichthys melanosticus	chloralkali plant	muscle	W 0.112	W 0.044	2.5X	Buhler et al. (1973)
Salmo fario	cinnabar refinery	kidney	W 0.357	W 0.00157	227.4X	Byrne et al. (1971)
Salmo trutta	wood pulp factory	muscle	W 3.58	W 0.21	17.0X	Underdal and Hastein (1971)
Stizostedion vitreum	chlorine plant	muscle	W 2.09	W 0.69	3.0X	Fimreite et al. (1971)
Stizostedion vitreum	chloralkali plant	muscle	W 15.74	W 1.50	10.5X	Fimreite and Reynolds (1973)
MOLLUSCS						
Anodonta grandis	chloralkali plant	foot	W 0.62	W 0.05	12.4X	Smith et al. (1975)
Mya arenaria	chloralkali plant	soft parts	W 3.59	W 0.93	3.9X	Fimreite et al. (1971)
Mytilus californianus	municipal waste water	digestive gland	W 0.15	W 0.05	3.0X	Eganhouse & Young (1976)
Mytilus edulis	industry	soft parts	W 0.425	W 0.115	3.0X	DeWolf (1975)
Patella vulgata	sewage discharge	soft parts	D 0.344	D 0.117	2.9X	Navrot et al. (1974)

(continued)

TABLE 21. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
CRUSTACEA						
Asellus aquaticus	paper pulp mill	whole	D 1.9	D 0.06	31.7X	Johnels et al. (1967)
Cancer magister	municipal sewage outfall	muscle	D 2.4	D 0.34	7.1X	Parsons et al. (1973)
Orconectes virilus	pulp mill chloralkali plant	muscle	W 1.14	W 0.2	5.7X	Sheffy (1978)
Orconectes virilus	pulp mill chloralkali plant	muscle	W 4.4	W 0.43	10.2X	Takeuchi et al. (1977)
"Crayfish"	chloralkali plant	muscle	W 2.18	W 0.18	12.1X	Buhler et al. (1973)
"Crab"	chloralkali plant	muscle	W 0.289	W 0.037	7.8X	Buhler et (1973)
Procambarus sp.	coal fly-ash basin		1.45	0.21	6.9X	Cherry et al. (1979)
INSECTS						
Isoperla sp.	paper mill	whole	W 2.40	W 0.072	33.3X	Johnels et al. (1967)
Sialis sp.	paper mill	whole	W 5.15	W 0.05	103.0X	Johnels et al. (1967)
Trichoptera	paper mill	whole	W 11.1	W 0.053	209.4X	Johnels et al. (1967)
ANNELID WORMS						
Helobdella sp.	paper mill	whole	W 3.1	W 0.025	124.0X	Jonels et al. (1967)
"Leech"	stream below town		W 0.403	W.00017	2,370.6X	Byrne et al. (1971)

(continued)

TABLE 21. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Lumbricus terrestris	chloralkali plant	whole less gut	W 1.29	W 0.041	31.5X	Bull et al. (1977)
HIGHER PLANTS						
Calamagrostis canadensis	gold smelter	leaf & stem	D 17.11	D 1.93	8.9X	O'Toole et al. (1971)
Nymphaea alba	paper mill	petiole, rhizome	W 0.52	W 0.016	32.5X	Johnels et al. (1968)
Prunus avium	factories	bark	W 59.0	W 0.063	936.5X	Byrne and Kosta (1972)
MOSSES						
Dicranum scoparium	exposed to fly ash near stacks	whole	1.13	0.066	17.1X	Huckabee (1973)
Fontinalis sp.	paper mill	whole	W 3.7	W 0.076	48.7X	Johnels et al. (1967)
Hylocomium splendens	urban and industry	whole	D 0.40	D 0.06	6.7X	Ruhling and Tyler (1973)
FUNGI						
Lactarius deliciosus	smelter	whole	D 20.6	D 0.75	27.5X	Kosta et al. (1974)

W = wet weight, D = dry weight, in ppm

recent collections of the same species from the same area. Marine algae also show ability to accumulate Ni but no studies were found which compared levels of environmental gradients.

For measuring environmental gradients of Ni, molluscs and crustacea have shown limited potential and data on fish are questionable. However, higher plants, mosses and lichens appear to have excellent capabilities.

TABLE 22. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF NICKEL BY ANIMALS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
FISH						
Catostomus commersoni	Ni smelter Ontario	muscle	W 13.2			Hutchinson et al. (1975)
Catostomus commersoni	none-New York	muscle		W 0.09	146.6X	Tong et al. (1972)
Esox lucius	Ni smelter	muscle	W 13.3			Hutchinson et al. (1975)
Esox lucius	none-New York	muscle		W <0.2	66.5X	Tong et al. (1972)
Esox lucius	none-Illinois	muscle		W 0.15	88.7X	Mathis and Cummings (1973)
Microstomus pacificus	sewage outfall	liver	D 2.6	D 1.4	1.86X	McDermott et al. (1976)
MOLLUSCS						
Buccinum undatum	ocean sludge dump	soft parts	D 8.5	D 0.6	14.2X	Mackay et al. (1972)
Patella vulgata	sewage outfall	soft parts	D 11.8	D 6.9	1.7X	Navrot et al. (1974)
Placopecten magellanicus	ocean sludge dump	soft parts	D 5.09	D 1.27	4.0X	Pesch et al. (1977)
CRUSTACEA						
Crangon allmani	ocean sludge dump	soft parts	D 92.0	D 15.0	6.1X	Mackay et al. (1972)
Pandalus montagui	ocean sludge dump	soft parts	D 70.0	D 25.0	2.8X	Mackay et al. (1972)

(continued)

TABLE 22. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
"Crayfish"	Ni smelter		D 39.0	D 5.0	7.8X	Hutchinson et al. (1975)
ECHINODERM						
Arbacia lixula	sewage pollution	soft parts	15.4	10.8	1.4X	Sheppard & Bellamy (1974)
ANNELID WORMS						
Allolobophora spp. and *Lumbricus terrestris*	gradient from highway	whole	D 34.5	D 25.2	1.37X	Gish and Christensen (1973)

D = dry weight, W = wet weight, in ppm

Selenium.

Selenium is widespread and relatively uncommon in some regions and may be abundant in other heavily mineralized regions. Eight species of biological organisms (Table 24) have been used to monitor environmental gradients of selenium, but in some studies there has been little correlation or even reverse correlation as in the case of the crab *Cancer anthonyi*.

Correlations have been made with gradients from a mercury mine, coal fly ash deposit in a swamp, mineralized area, phosphate processing plant and with growing plants on fly ash and soil. Correlations of spanish moss distribution showed three sites (with 1.0 ppm dry weight) in industrial areas, compared with non-detected in over 100 other sites.

There are many observations of high levels in plants growing in highly seleniferous soils, and even grass having higher levels when growing close to *Astragalus* accumulators of Se.

The best organisms for measuring environmental gradients of Se appear to be plants such as the grass *Agropyron* and sagebrush *Artemisia tridentata*. There are many species of plants with a high capability for accumulating Se that would probably be more effective, such as *Astragalus*, *Aster*, Haplopappus, Stanleya, and perhaps wheat.

TABLE 23. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF NICKEL BY PLANTS

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
HIGHER PLANTS						
Acer rubrum	Ni smelter	leaf	D 123.0	D 14.0	8.8X	Hutchinson and Whitby (1973)
Anacharis canadensis	Ni smelter	leaf	D 510.0	D 18.0	28.3X	Hutchinson et al. (1975)
Artemisia tridentata	phosphate process plant	branch, flower	D 30.0	D 15.0	2.0X	Gough and Severson (1976)
Betula papyrifera	Ni smelter	leaf	D 157.9	D 61.5	2.6X	Hutchinson and Whitby (1974)
Comptonia peregrina	Ni smelter	leaf	D 112.8	D 17.4	6.5X	Hutchinson and Whitby (1974)
Cornus canadensis	Ni smelter	leaf	D 47.7	D 21.7	2.2X	Hutchinson and Whitby (1974)
Deschampsia flexuosa	Ni smelter	leaf	D 902.0	D 37.0	24.4X	Hutchinson and Whitby (1973)
Equisetum palustre	Ni smelter	stem	D 124.8	D 56.4	2.2X	Hutchinson and Whitby (1974)
Festuca rubra	industrial area	stem & leaf	D 15.0	D 6.0	2.5X	Goodman and Roberts (1971)
Festuca sp.	highway	stem & leaf	D 8.8	D 2.05	4.3X	Lagerwerff and Specht (1970)

(continued)

TABLE 23. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Nuphar variegatum	Ni smelter	leaf	D 47.0	D 8.0	5.9X	Hutchinson et al. (1975)
Pinus banksiana	Ni smelter	needle	D 108.6	D 23.6	4.6X	Hutchinson and Whitby (1974)
Populus grandidentata	Ni smelter	leaf	D 156.6	D 16.4	9.5X	Hutchinson and Whitby (1974)
Potamogeton sp.	Ni smelter	leaf	D 480.0	D 50.0	9.6X	Hutchinson et al. (1975)
Pteridium aquilinum	Ni smelter	leaf	D 43.1	D 17.0	2.5X	Hutchinson and Whitby (1974)
Silene maritima	serpentine area	shoot	A 405.0	A 25.0	16.2X	Shewry and Peterson (1976)
Thymus drucei	serpentine area	shoot	A 1,103.0	A 53.0	20.8X	Shewry and Peterson (1976)
Tillandsia usnoides	industry, highways incineration	whole	A 200.0	A 7.0	28.5X	Shacklette and Connor (1973)
Vaccinium agustifolium	Ni smelter	leaf	D 92.3	D 14.4	6.4X	Hutchinson and Whitby (1974)
MOSSES						
Dicranoweisia cirrata	steelworks (transplants)	whole	D 35.2	D 1.0	35.2X	Pilegaard (1979)

(continued)

TABLE 23. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Homalothecium sp. and 4 spp. mosses	rural area increase 1951-1973	whole	D 4.7 (1973)	D 3.3 (1951)	1.4X	Rasmussen (1977)
Hylocomium splendens	industry	whole	D 7.0	D 1.8	3.9X	Ruhling and Tyler (1973)
Hypnum cupressiforme	increase 1870-1969	whole	D 9.1 (1969)	D 4.0 (1870)	2.3X	Ruhling and Tyler (1969)
LICHENS						
Hypogymnia physodes	steelworks (transplants)	whole	D 27.5	D 3.0	9.2X	Pilegaard (1979)
Lecanora conizaeoides		whole	D 47.0	D 4.3	10.9X	Pilegaard (1978)
Peltigera rufescens	steel smelter	whole	D 38.5	D 10.3	3.7X	Seaward (1973)
Stereocaulon paschale	Ni smelter	whole	D 180.0	D 26.0	6.9X	Nieboer et al. (1975)
Umbilicaria deusta	Ni smelter	whole	D 220.0	D 37.0	5.9X	Nieboer et al. (1975)

D = dry weight, W = wet weight, in ppm

Tin

There are relatively few data on the levels of Sn in plants and animals. This is probably due to Sn being localized, not widespread nor commonly found, and to the fact that Sn is not concentrated to any extent in animals, and especially due to the great difficulty in accurately measuring Sn in biological tissues. Only comparatively recently could Sn be measured with confidence, so that all earlier (at least before 1960) measured concentrations are suspect. This severely delimits the amount of data available, especially for animals. No animal species are known to have been used to measure environmental gradients of tin. Eleven species of higher plant (Table 25)

TABLE 24. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF SELENIUM

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Bufo bufo	mercury mine	liver	W 3.2	W 0.73	4.4X	Byrne et al. (1975)
Cancer anthonyi	industrial and urban waste	muscle	W 5.14	W 15.66	-3.0X	Fowler et al. (1975)
Libellula sp.	flyash swamp	whole	3.0	0.85	3.5X	Cherry et al. (1979)
Zapus princeps	mineralized area	hair	2.0	ND	---	Huckabee et al. (1972)
Agropyron sp.	phosphate processing plant	leaf & stem	D 1.2	D 0.1	12.0X	Gough and Severson (1976)
Artemisia tridentata	phosphate processing plant	leaf & stem	D 1.2	D 0.06	20.0X	Gough and Severson (1976)
Brassica oleracea capitata	grown in 7 percent flyash	head	D 145.0	D 21.0	6.9X	Furr et al. (1977)
Tillandsia usnoides	industrial site	whole	D 1.0	D ND	---	Shacklette and Connor (1973)

D = dry weight, W = wet weight, in ppm

have been used to measure environmental gradients of Sn around Sn smelters, mining areas, slime holding ponds for Sn waste, slag heaps, and also for comparing the effect of sludge fortified soil with normal soil. For measuring environmental gradients of Sn, higher plants have been effective and certain species presently appear to have promise for biological monitoring.

Vanadium

Vanadium is widespread and is rarely concentrated in high quantities, except for local pollution caused by man. Ten studies have been conducted using biological organisms for monitoring environmental gradients of vanadium (Table 26).

TABLE 25. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF TIN

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
Avicennia alba	mine pollution	leaf	D 10.8	D 1.4	7.7X	Peterson et al. (1979)
Avicennia officinalis	mine pollution	leaf	D 10.2	D 0.9	11.3X	Peterson et al. (1979)
Beta vulgaris cicla	soil sludge fortified	leaf & stem	D 100.0	<0.5	200.0X	Furr et al. (1976)
Bruguiera caryophylloides	mine pollution	leaf	D 9.4	D 1.3	7.2X	Peterson et al. (1979)
Carapa moluccensis	mine pollution	leaf	D 9.6	D 1.5	6.4X	Peterson et al. (1979)
Desmodium triflorum	Sn slime pond	leaf	D 9.8	D 1.8	5.4X	Peterson et al. (1976)
Ischaemum muticum	Sn slime pond	leaf	D 8.6	D 2.6	3.3X	Peterson et al. (1976)
Melastoma malabathricum	Sn slime pond	leaf	D 6.8	D 2.9	2.3X	Peterson et al. (1976)
Mimosa pudica	Sn smelter flue	leaf	D 138.0	D 8.9	15.5X	Peterson et al. (1976)
Rhizophora conjugata	mine pollution	leaf	D 15.0	D 2.4	6.3X	Peterson et al. (1976)
Tridax procumbens	Sn smelter flue	leaf	D 700.0	D 21.7	32.2X	Peterson et al. (1976)
Tillandsia usnoides	Sn smelter	whole	A (20-30)	D <20		Shacklette and Connor (1973)

D = dry weight, W = wet weight, in ppm

TABLE 26. BIOLOGICAL MONITORING OF ENVIRONMENTAL GRADIENTS OF VANADIUM

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MAMMALS						
Cavia porcellus	fed swiss chard grown on sludge-fortified soil	kidney	D 4.9	D 0.3	16.3X	Furr et al. (1976)
FISH						
Paralabrax clathratus	steam plant effluent	muscle	D 3.25	D 1.8	1.8X	Stapleton (1968)
MOLLUSCS						
Placopecten magellanicus	acid wastes and sewage sludge dump	soft parts	D 38.1	D 16.4	2.3X	Pesch et al. (1977)
PLANTS						
Agropyron sp.	phosphate processing plant	leaf & stem	A 300.0	A 15.0	20.0X	Gough and Severson (1976)
Artemisia tridentata	phosphate processing plant	leaf, stem & flower	A 700.0	A 30.0	23.3X	Gough and Severson (1976)
Tillandsia usnoides	atmospheric pollution	whole	A 500.0	A 15.0	33.3X	Shacklette and Connor (1973)
LICHENS						
Hypogymnia physodes	steelworks and foundary	whole transplants	D 10.7	D 4.7	2.3X	Pilegaard (1979)
Lecanora conizaeoides	steelworks and foundary	whole	D 169.0	D 5.4	31.3X	Pilegaard (1978)

(continued)

TABLE 26. (Continued)

Organism	Pollution Source	Tissue	Exposed	Control	Increase Contam.	Authority
MOSS						
Dicranoweisia cirrata	steelworks and foundary	whole transplant	D 19.3	D 3.9	4.9X	Pilegaard (1979)
Five species of mosses	increase in V from 1951-1975	whole	D 12.0 (1975)	D 6.0 (1951)	20.0X	Rasmussen (1977)

D = dry weight, W = wet weight, in ppm

While over 300 species of plants and animals have been measured for content of V, most of these are not related to the environmental levels and many are earlier determinations, the accuracy of which is suspect. There are many evaluations for tunicates which are known to concentrate vanadium.

Guinea pigs were used to compare the effect of growing swiss chard on natural and sludge-amended soil. Animals fed swiss chard grown on sludge-amended soil had a much higher level of vanadium in the kidneys. Calico bass collected in the effluent of a steam plant had higher vanadium levels in muscles than did controls. Sea scallops have also been used to measure an environmental gradient of vanadium.

Bunch grass and sage were used to study environmental gradients from a phosphate processing plant. The leaves and stems of plants 2.5 km from the plant had from 20 to 23 times the V content compared with controls 32 km downwind from the factory site. There was good negative correlation of vanadium with distance from the factory. Spanish moss showed high concentrations in vanadium in areas where high rates of vehicular and industrial emissions occurred or were expected. No other higher plants are known to have been used to measure environmental gradients of vanadium. Two species of lichens and one species of moss were used to measure environmental gradients and five species of mosses were used to show increase of vanadium with time.

Potential Monitoring Organisms

Selection of monitoring organisms was accomplished using a three-step procedure. First, data on concentrations of the trace elements in the various species of organisms were compiled in comparable terms (Volume 2). Second, the data were evaluated with regard to a) species which show the capability to bioaccumulate and bioconcentrate the elements and retain or store them in organs or tissues suitable for monitoring, b) effectiveness of use of various species for monitoring environmental gradients of the trace metals, c) biomagnification and biominification in food chains, and d) biotransformation of trace elements to other forms and compounds. This information allowed a tentative selection of potential monitoring organisms. Third, selections can then be made on the basis of selection criteria and the needs and priorities presented previously.

Data in Volume 2 have been carefully reviewed, and tentative baseline reference concentrations for each group of organisms for each trace metal have been estimated (Tables 27 through 40). These baseline reference ranges are based on concentrations in organisms in areas where there is little or no pollution, or in areas where heavy pollution has not been reported. These figures are tentative and subject to revision when more detailed studies on concentrations of trace metals in the environmental background have been measured. These tentative reference baseline data are useful in comparing with concentrations of trace elements in organisms in heavily polluted areas, and with the maximum concentrations shown in Tables 27 through 40.

Selecting organisms for biological monitoring based only on ability to accumulate high levels could be erroneous. For example, some organisms such as tunicates have the ability to bioconcentrate and sequester vanadium into storage tissue in very high concentrations. This may be accomplished in areas with only the small normal background levels in vanadium in seawater. Also some large predators such as pike, tuna and seals have the capability to continue accumulating mercury and storing it in muscle and other tissue for many years so that the concentration of mercury can be mainly a function of age and size instead of a direct relationship to environmental levels of mercury.

Each order or major taxonomic group of organisms is discussed with regard to selection of potential monitoring organisms for each of the selected trace metals. The tentative selections take into account the need for monitoring in the vicinity of man; in urban, industrial and different rural areas, and in freshwater streams and lakes and coastal, estuarine, and marine areas.

Antimony

The published data available on antimony concentrations in plants and animals includes 158 species of which 129 species are animals and 29 species are plants (Table 27). The data are relatively limited and frequently represent only one or a few measurements with little comparative data or information on levels of antimony or component parts of the organisms. The results do not show correlation with pollution or contamination, and some sporadic data with high levels are not correlated with any known high environmental levels of Sb. It is therefore difficult to select monitoring organisms that would have good potential for biological monitoring of antimony.

Mammals and Birds

Several species of mammals show fairly high levels of antimony in hair which would appear to be the best tissue to use for monitoring. Higher

TABLE 27. SUMMARY OF ANTIMONY LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	17	D? (0.0-2.5)	D? 13.0	hair	data sparse
Birds	4	<0.2		feather	data sparse
Marine fish	34	W (0.02-0.2)	W 0.61	muscle, liver	
Freshwater fish	16	W (0.003-0.1)	W 0.86	muscle, liver	data sparse
Molluscs	21	D (0.01-0.2)	D 0.92	soft parts	data sparse
Crustacea	13	----	W 6.1		data sparse
Echinoderms	10	----	D 5.5		data sparse
Lower animals	14	----	W 1.2		data sparse
Higher plants	13	D (0.0-0.6)	D 38.0	leaf	data sparse
Algae	16	D (0.02-0.23)	D 7.87	whole	data sparse
Total	158				

D = dry weight, W = wet weight, in ppm

levels of antimony have been shown in the skeleton, liver and spleen in laboratory studies. In guinea pigs, the adrenals had the highest level of antimony as reported in Table 11, on biological monitoring of environmental gradients of Sb. Elk and deer hair showed high levels of antimony. Birds have not been studied and antimony levels in feathers of four species were low. No species of mammals or birds have been selected for potential use in monitoring antimony.

Marine and Freshwater Fish

Thirty-four species of marine fish have been measured for Sb concentrations. None of the species had high levels (maximum was 0.61 ppm wet weight). There is evidence of predatory species having lower levels than prey species indicating biominification in the food chain. The data on freshwater fish are less extensive than marine fish and no species had high levels of antimony. No species of marine or freshwater fish have been selected for potential use in monitoring antimony.

Molluscs, Crustacea and Lower Animals

Molluscs, crustacea and other lower animals do not show any marked ability to accumulate Sb. The oyster *Ostrea sinuata* in New Zealand was reported by Brooks and Rumsby (1965) to have 80.0 ppm dry weight of Sb in muscle. This was determined in a single sample using spectrographic arcing with a minimum detection limit of 30 ppm for Sb. This was not included in selecting organisms for monitoring. The maximum concentration reported is for the octopus, with 0.92 ppm wet weight but the average maximum was about 0.2 ppm wet weight. One mollusc was used to measure an environmental gradient of Sb but the results were of borderline significance, the same as the results for crayfish.

The sea urchin *Arbacia lixula* had 5.5 ppm dry weight which is surprisingly high for Sb (Papadopoulou et al. 1976). Amphipods had up to 6.1 ppm wet weight (Van As et al. 1975). These might be considered for monitoring, but more data are needed.

Higher Plants

While available data on concentrations of antimony in higher plants are limited to 13 species, there is information on ability of some species to accumulate Sb when exposed. Swiss chard accumulated high levels (to 11.5 ppm dry weight) when grown in sludge amended soil. In the area around a gold smelter, northern reed grass and a wild rose accumulated high levels. Tobacco also had high levels of Sb. Swiss chard and wild rose were successfully used to measure environmental gradients. Certain higher plants appear to have a potential for use as biological monitors of Sb with the best known tissues being leaves and fruit.

Algae

Marine algae are not known to accumulate high levels, have not been used to measure environmental gradients, and none are presently considered for monitoring Sb.

In summary, no animals except perhaps the sea urchin and copepods appear to have potential value for biological monitoring of antimony based on presently available data. Several species of higher plants that accumulate significant levels have been used successfully for measuring environmental gradients and have promise for biological monitoring of antimony. No species of algae appear to be suitable organisms.

Arsenic

A total of 652 species of organisms have been analyzed for arsenic including 428 species of animals and 224 species of plants (Table 28). Arsenic concentrations are not biomagnified in the food chains (Table 9) except at lower levels according to Penrose (1974) and Klumpp and Peterson (1979). In food chain studies, Lunde (1970) showed that filterfeeders

TABLE 28. SUMMARY OF ARSENIC LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	24	W (0.1-2.0)	W 19.0	hair, muscle, liver	hair good as indicator
Birds	25	W (<0.05-1.76)	W 2.5	liver, kidney, etc.	data sparse
Reptiles	2	W (0.05-0.2)	----	egg	data sparse
Amphibia	5	W (0.021-0.444)	----	liver	data sparse
Marine fish	135	W (0.1-11.0)	D 307.0	liver, muscle	fair indicator
Freshwater fish	103	W (0.0-2.0)	W 4.5	liver, muscle	not good indicator
Molluscs	52	W (0.5-40.0)	W 119.0	soft parts	good indicator
Crustacea	48	W (0.02-50.0)	W 174.0	muscle, etc.	fair indicator
Insecta	1	----	----	----	need more data
Echinoderms	11	D (1.3-10.0)	? 50.9	----	data sparse
Lower animals	22	D (0.15-19.0)	D 72.0	whole	data sparse
Higher plants	162	D (<1.0-5.0)	D 4,130.0	all parts	good indicator
Moss	2	----	D 99.0		need more data
Algae	60	D (0.25-80.0)	D 180.0	all parts	good indicator
Total	652				

D = dry weight, W = wet weight, in ppm

averaged 9.1 ppm, feeders on zooplankton 3.4 ppm, predators on benthic organisms 5.0 ppm, and predators on fish had 2.2 ppm in muscle. The concentrations may decrease with ascending trophic levels. When animals and humans were fed shrimp and lobster containing high levels of arsenic, it was excreted rather rapidly, mainly in the urine.

Mammals

Mammals which appear to have promise as biological monitors of As include cows, horses, and sheep. The tissue of choice is the hair or mane. Cow hair and horse manes were effective in measuring environmental gradients of arsenic (Table 12). When sheep were fed high levels of arsenic in Elodea by Lancaster et al. (1971), the wool contained 12.6 ppm dry weight while the kidney had 3.76 ppm and liver 3.07 ppm wet weight. Cows, horses, and sheep were said to have died near a Cu smelter in Germany (Bischoff and Haun 1939) due to arsenic poisoning.

Birds

Birds do not appear to accumulate arsenic in any tissues including eggs. Some species are predators on crustacea, molluscs and marine fish which often have high levels of As.

No birds have been found to be suitable for measuring environmental gradients of As. The tissue with the highest levels was liver (2.2 ppm wet weight) and to 12.0 ppm in chicken liver and from As overdose (Baker and Parker 1969). No species of birds are recommended for biological monitoring of As.

Reptiles and Amphibia

There are insufficient data to recommend any species for biological monitoring. Frog liver was found to be suitable for measuring the environmental gradient of As near a mercury mine in Yugoslavia (Byrne et al. 1975).

Fish

Arsenic levels have been measured in 135 species of marine fish. Four species have been used to measure environmental gradients of As. Muscle and liver tissue contained the highest levels. Certain marine fish can be considered to have some promise for biological monitoring, but no species have been selected with good potential. Most species of freshwater fish have relatively low levels and none have been used to measure environmental gradients of As. However, some of the measurements by Ellis et al. (1941) and some earlier data reported in Vinogradov (1953) have higher levels than most recent determinations. No freshwater species of fish has been selected for potential biological monitoring organisms and they do not appear to be good indicators of As.

Molluscs

Molluscs accumulate large concentrations of As, frequently to 40 ppm wet weight. While they have not been used to measure environmental gradients of arsenic, various molluscs may show high concentrations when they are in heavily polluted areas. Some of the highest values are by Chapman (1926) who measured As in molluscs from the lower Thames River in Great Britain. The soft tissue appears to have the highest levels but few studies have been made on the levels of the component tissues and organs.

The species with some potential for biological monitoring could include *Mytilus edulis*, *Buccinum undatum*, *Crassostrea angulata* and *Littorina littorea*.

Crustacea

Crustacea may accumulate or concentrate very high levels of As. The crab *Cancer anthonyi* was used to measure environmental gradients of As and various crustacea in polluted areas had high concentrations. Nearly all of the tissues show high levels except the shell or carapace. Muscle, gills, hepatopancreas, digestive gland, gonads, eggs and spawn may all show high levels. Crabs, especially *Cancer* and *Mursia*, lobster, shrimps and prawns appear to have some potential as biological monitoring organisms for arsenic.

Lower Invertebrates

There are insufficient data to be able to recommend any lower invertebrates for biological monitoring of As, however, one species of echinoderm was used to measure an environmental gradient. Many of the lower invertebrate species measured had fairly high levels of As.

Higher Plants

Some angiosperm plants accumulate arsenic in very high concentrations. Certain plants adapted to growing on mine waste, in smelter areas, or in geothermal springs may have high concentrations. Six species of higher plants have been used to measure environmental gradients, and others are excellent indicators of high levels of As. Some of the tissues with highest levels are the leaf and stem and occasionally the roots and seeds.

Higher plants have real value as potential monitoring organisms for arsenic. These include *Agrostis spp.*, *Artemisia spp.*, *Calluna sp.*, *Jasione sp.*, *Picea alba*, *Pseudotsuga menziesii*, *Rosa acicularis* and a variety of freshwater aquatic plants.

Algae

Marine algae may accumulate high concentrations and one species was used to measure an environmental gradient of As. Most algae have fairly high levels in unpolluted areas and in As polluted areas. Algae appear to be good biological monitors and some with potential are *Ascophyllum nodosum*, *Cystophyllum sp.*, *Laminaria spp.* and *Macrocystis pyrifera*.

In summary, the hair of cows, horses and sheep, the muscle and liver of certain marine fish, several species of molluscs and various crustacea especially certain crabs, lobsters, shrimp and prawns appear to have the best potential for biological monitoring of As. Various plants including certain grasses, gymnosperms and various freshwater aquatic plants and marine algae also have good potential as monitoring organisms for As.

Beryllium

Only 76 species of organisms were found that had been measured for beryllium concentration, including 31 species of animals and 45 species of plants (Table 29).

TABLE 29. SUMMARY OF BERYLLIUM LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	3	----	<3.0	liver	data sparse
Birds	10	----	<1.0		data sparse
Fish	8	----	A 1.78	gut and muscle	data sparse
Invertebrates	10	----	A 1.15	"flesh"	data sparse
Higher plants	33	A (0.01-1.0)	A 30.0	leaf and fruit	
Lichens, mosses and fungi	9	<1.0	A 6.0	----	data sparse
Algae	3	A (0.01-0.05)	A 1.02	----	data sparse
Total	76				

D = dry weight, W = wet weight, in ppm

Mammals and Birds

All of the levels of Be for mammals and birds are low, reflecting the lack of absorption and lack of accumulation and biomagnification of this trace element in organisms. No species show potential for monitoring Be.

Fish

Limited data on Be in fish indicates that the gut and muscle have low concentrations of Be. No species appear suitable as potential biological monitors.

Higher Plants

Some species of plants accumulate Be and are used as indicator plants with up to 30.0 ppm ash weight. The best Be accumulator plants known at present appear to be *Betula*, *Carya*, *Pinus*, *Populus*, *Salix* and *Tillandsia usnoides*. In addition, alfalfa, peas, ladino clover and corn have shown capability to accumulate Be when grown experimentally and exposed to Be.

Lower Plants

"Bryophytes" have been shown to contain up to 6.0 ppm ash weight and might be considered for biological monitoring. More data on Be levels in lower plants are needed.

Boron

Boron is accumulated in fairly high concentrations in many of the 168 species of biological organisms studied. Sixty species of animals and 108 species of plants have been measured (Table 30).

Mammals, Birds and Fish

Only two species of mammals, no species of birds, and nine species of fish have been analyzed for boron. Much of the data on fish are older and there is wide variation. No vertebrate animals are recommended for monitoring.

Lower Animals

There are few data for molluscs, crustacea and echinoderms and there is wide variation with some levels quite high.

Coelenterates, particularly corals, have fairly high levels of boron, rather consistently from 40.0 ppm to 100.0 ppm dry weight, but nothing is known of their uptake in polluted areas. There are insufficient data to recommend any invertebrate animals for biological monitoring.

Higher Plants

Some higher plant species accumulate high levels of boron and are excellent indicator plants. Three species of plants have been used for measuring environmental gradients of boron. Since boron occurs as deposits in desert areas, many desert plants contain high concentrations. A large number of species could be selected on the basis of high accumulation, having been used for prospecting, and for measuring environmental gradients of boron. Some of these are proposed for biological monitoring plants, but no species of mosses, lichens or algae are recommended for monitoring boron.

TABLE 30. SUMMARY OF BORON LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	2	----	D 5.0	bone	data sparse
Fish	9	----	A 150.0	stomach	data sparse
Molluscs	5	----	A 420.0	----	data sparse
Crustacea	10	----	A 760	----	data sparse
Echinoderms	6	----	----	----	data sparse
Lower animals	28	D (40.0-80.0)	D 500	coral	data sparse
Higher plants	95	D (20-100)	D 1,588	leaf	good bioindicator
Bryophytes and fungi	2	----	----	----	data sparse
Algae	10	----	D 120	----	data sparse
Bacteria	1	----	----	----	data sparse
Total	168				

D = dry weight, W = wet weight, in ppm

Cadmium

The accumulation levels of cadmium in plants and animals have been fairly well documented and over 1,040 different species have been measured. This includes 698 species of animals and 342 species of plants. Table 31 shows the numbers of species of each major group of organisms, tentative baseline data for uncontaminated or low contamination areas, and maximum levels in the tissues or organs having highest levels of Cd.

Mammals

Mammals accumulate cadmium in certain tissues or organs. Several species of mammals have been used effectively to monitor environmental gradients of Cd in terrestrial areas.

TABLE 31. SUMMARY OF CADMIUM LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	50	W (0.01-<10.0)	W 410.0	kidney	high in seal and sea lion
Birds	38	W (0.1-<12.0)	W 51.35?	liver, kidney	good indicator
Reptiles	3	----	9.87	----	more data needed
Marine fish	228	W (0.2-<2.0)	W 83.0	liver	fair indicator
Freshwater fish	89	W (0.0-2.0)	W 68.9	kidney & muscle	fair indicator
Molluscs	126	W (0.0-10.0+)?	W 329.0 D 1,162.7	stomach, digestive gland	very good indicator
Crustacea	66	W (0.0-13.0)	D 124.8	whole	good indicator
Insects	35	D (<0.05-10.0)?	D 149.7	----	need more data
Echinoderms	21	D (0.03-12.0)?	D 46.3	----	need more data
Lower invertebrates	42	D (0.25-8.0)	D 12.6	----	need more data
Higher plants	210	D (0.01-5.0)	D 257.0	leaf, grain	good indicator
Mosses	27	D (<0.1-5.0)	D 148.0	whole	good indicator
Lichens	26+	D (0.1-10.0)	D 320.0	whole	good indicator
Fungi	2	----	D 5.34	----	need more data
Algae	77	D (0.0-8.0)	D 220.0	whole	good indicator
Total	1,040				

D = dry weight, W = wet weight, in ppm

The mammalian tissues that appear best for sampling are hair or mane, kidney and liver. Hair can be obtained without damage to the animal and standardized methods of sampling are available. The kidney is the site of greatest accumulation or concentration followed by the liver. Cow's milk appears to have some suitability for monitoring based on the limited data available. Other tissues such as bone, muscle, brain, heart and fat do not appear to be suitable.

Little is known about confounding variables in the bioaccumulation of Cd in mammals but age could be a factor. Mature ground squirrels and gray squirrels had about four to five times greater Cd concentrations than immatures (Munshower 1972, and McKinnon et al. 1976). The half life of Cd in mammals ranges from 200 days in mice to 2 years in monkeys.

Species of mammals with potential as biological monitors include domestic animals such as cows, horses, rabbits, pigs and sheep. In addition, wild species of rodents including certain types of mice, squirrels, ground squirrels and cottontail rabbits show potential for monitoring. Seals, sea lions and walrus accumulate high levels of Cd in the kidney and liver and are also potential monitors for marine areas.

Birds

Birds accumulate fairly high levels of cadmium, especially in the kidney and liver, the same as mammals. However, only one species of bird has been used to measure environmental gradients of Cd. Starlings have been analyzed extensively in the United States at 56 sites in 44 states. However, the levels of Cd in the birds (minus wings, feathers, skin, beak and feet) was quite low. Measurements were made during 1971 (Martin and Nickerson 1973) and there was a slight increase in 1973 (White et al. 1977). Starlings in six cities in 1971 had over 0.1 ppm Cd wet weight but in 1973 dropped below 0.07 ppm, while concentrations in six other sites nearly doubled from less than 0.06 ppm in 1971 to over 0.11 ppm in 1973. Use of starlings in this manner does not appear to be a very effective biological monitoring species for Cd. Analyses of the kidney and liver would probably be more effective. Brown pelican livers from California were several times higher than from Florida, Georgia or South Carolina, but bone and muscle tissue were not different.

In general, predatory birds such as fish-eating marine birds appear to have the highest cadmium contents. Scavenger species such a gulls also have high levels. Certain terrestrial birds such as chickens, grouse and pheasants also accumulate Cd. No data are available on Cd concentrations in pigeons. These species deserve some consideration as potential biological monitoring organisms, but more information is required on retention time, biological halflife, feeding habits and migration before birds can be used effectively for biological monitoring of Cd.

The most important tissues of birds for monitoring Cd are the kidney and liver. There are a few instances of fairly high levels in bone, brain and muscle, but these appear to be exceptions. The use of eggs, feathers, wings and muscles do not appear to be suitable tissues for monitoring Cd in birds.

Fish

Marine fish have been well studied with 228 species measured for Cd content. Some species might be suitable for monitoring, especially larger predators such as marlin, but a number of other more common species such as dover sole, kelp, bass, flounder, plaice and pollack show ability to accumulate Cd. Some sharks, rays and skates also show high levels in some tissues.

The tissues with highest levels are kidneys, gills, livers, and skin, with some muscle tissue being fairly high. However, muscle tissue has been very well tested and is usually comparatively low in Cd.

Apparently no marine fish have been used to monitor environmental gradients of Cd, but garfish and dover sole show higher levels in polluted areas. Studies on the flathead flounder *Platycephalus bassensis* in Port Phillips Bay, Austrialia (Phillips 1977) indicate use of liver to measure Cd might be justified since there was some correlation of Cd levels with pollution levels in three sites. More research is needed for selecting any marine fish for biological monitoring.

Freshwater fish have been well studied in numerous states in the United States, but much of the data are not comparable and different tissues were used. The National Pesticide Monitoring Program compiled Cd levels in fish from 92 rivers and streams in 46 states for 1972. Cd levels were mostly from less than 0.05 to 0.5 ppm wet weight with a maximum of 1.0 ppm in five sites.

Freshwater fish usually have relatively low levels of Cd. However, in highly polluted rivers such as the Hudson River, carp, golden shiner, dace and bass had high levels. In addition, species of trout, suckers and catfish showed some Cd accumulation as well as goldfish and lake herring.

The highest levels of Cd are in the kidney and liver. Most studies have used the muscle or whole fish so there are limited data on comparison of Cd concentrations in various tissues. However, the Cd content of bone in rainbow, brook and brown trout was surprisingly high with maximum levels from 19.9 to 26.4 ppm wet weight of Cd. More data are needed for freshwater fish in highly polluted areas. No species are known to have been successfully used to monitor environmental gradients of Cd except measurements of fish in the Hudson River compared with unpolluted areas. No species can presently be recommended for monitoring Cd in freshwater.

Molluscs

Molluscs probably fit the recommended criteria for selection of monitoring organisms for Cd better than any others. They have been well studied with 126 species analyzed. They have been used rather extensively to monitor environmental gradients of Cd (Table 13). Most of the species used are in marine areas or brackish estuaries, but some freshwater and even one terrestrial species (*Helix*) have been used. Molluscs appear to be able to accumulate or concentrate Cd and store it in quantity without serious harm.

In freshwater lakes, ponds and streams, several species of clams and mussels have been shown to accumulate Cd, but more research is needed to select the best species for monitoring. The pulmonate terrestrial snail *Helix aspersa* has been found to be a good monitoring organism and Cd was concentrated in the digestive gland, kidney and crop. The digestive gland appears to concentrate Cd more than any other tissue or organ in the molluscs studied. The kidney, liver and viscera may contain high levels as may the heart and muscle in certain species. The shell usually contains low levels. In the squid and cuttlefish the liver concentrates Cd.

Molluscs are probably the best animal organisms for use in biological monitoring for Cd.

Other Animals

Anthropods have been fairly well studied with about 100 species tested. Of the crustacea, barnacles appear to have the best potential for monitoring Cd but more information is required for correlating with pollution levels. Decapod crustacea may have fairly high levels but because of the rapid turnover of metals in these organisms, they do not appear to be useful indicators of trace metal pollution (Martin 1974, Wright 1976, and Phillips 1977). No studies are known of attempts to use crustacea to measure environmental gradients of Cd.

Insects may have some potential as monitors. In Missouri, fruitflies *Drosophila spp*. have been used by Lower (1974) to measure environmental gradients of Cd in relation to distance from a smelter. Correlations appear good and *Drosophila* could be considered as potential organisms for monitoring gradients of Cd under certain conditions.

Echinoderms may have limited potential as monitors but the present data are too limited. The Annelida appear to have somewhat greater promise. Levels of Cd in earthworms showed a fairly good correlation with distance from a highway and, in experiments with sludge amendment of soil, earthworms had up to 15 times more cadmium than controls. More data are required to prove the real potential of earthworms as soil monitoring organisms. The marine clam worm *Nereis diversicolor* has been studied by Bryan and Hummerstone (1973). It might be used to monitor sediments but not the water. The Cd is not regulated in the worm but is roughly proportional to Cd in the surrounding sediments.

Higher Plants

Plants do not normally accumulate very high concentrations of Cd and no hyperaccumulators (1,000 ppm dry weight) are known as for Ni and some other trace metal elements. The amount of Cd in leaves and stems is usually under 10 ppm, except around smelters where up to 50 ppm dry weight may be present. However, for unwashed elm leaves with 30 to 55 ppm dry weight washing with detergent removed 78 percent of the Cd, showing that the metal was deposited from air onto the leaf surface. One of the highest known Cd concentrations was found on bunch grass (250 ppm) and on sagebrush with 130 ppm dry weight, downwind from a phosphate processing plant in Idaho.

The aquatic naiad *Najas guadalupensis* increased from 71 ppm to 4,357.9 ppm ash weight when the Cd in the water was increased to 0.9 ppm Cd. In an experiment with wheat, the Cd in grain increased from 0.067 ppm in the control to 257.0 ppm dry weight in plants grown in soil with 58 tons of sewage sludge added per hectare. With 6.5 tons of sludge/hectare the Cd level in the grain was 119.0 ppm. This and other experiments show that various species of plants are capable of absorbing and accumulating high levels of Cd. Many species of plants have been used successfully for monitoring environmental gradients of Cd.

There are a large number of species which have the capability to absorb and retain quantities of Cd so that they can be considered in selecting potential monitoring organisms. The cutivated plants include onions, oats, parsnip, lettuce, tomato, wheat, corn, eggplant, ryegrass, carrot, bean, potato, barley and radish. Wild plants include sagebrush, *Clintonia*, naiad, spanish moss, and the trees cedar, mulberry, spruces, elm, hickory and poplar. Other plants can also be considered, especially aquatic plants such as water milfoil, *Myriophyllum*, which had a coefficient of accumulation of Cd of 10,110 which was the highest tested (Makhonina and Gileve 1968).

The tissues used include leaf, stem, branch, wood, bark, blossom, grain and fruit, bulb, tuber, root, or the top or whole plant. All of the tissues appear to be suitable, but the highest levels of Cd have been found in and/or on leaves and bark and in grain. The problem of external contamination of leaf, twig and branch and bark contamination by airborne Cd must be considered in a biological monitoring program. Data from both unwashed and washed leaves could be of value in determining total amount, source and pathway of pollution.

Lower Plants

Mosses are excellent Cd accumulators and have been used effectively in measuring environmental gradients of Cd. One of the highest known levels of Cd in mosses was found in *Eurhynchium praelongum* with 148 ppm dry weight of Cd at 2.9 miles downwind from a zinc smelter in Bristol, Great Britain (Burkitt et al. 1972). Cd concentration in *Hypnum compressiforme* has been used extensively as an index to airborne cadmium pollution in Sweden. The normal Cd concentration in unpolluted areas is 0.7 to 1.2 ppm dry weight and in the center of a city with a storage battery factory that released Cd, the moss had 81.7 ppm (Ruhling 1971 and Shacklette 1972). In the area around a Zn Pb smelter at the site of greatest pollution, introduced moss specimens increased from a background of 2.0 ppm to 337.0 ppm dry weight of cadmium after two weeks exposure (Little and Martin 1974). Various other mosses have been used for monitoring Cd environmental gradients including *Hylocomium splendens* and *Pleurozium schreberi*.

Lichens are excellent Cd accumulators (up to 320.0 ppm dry weight) and have been used to measure environmental gradients (Table 14). Various species of *Cladonia*, *Parmelia*, *Umbilicaria*, *Lasallia*, *Micaria* and *Verrucaria* have potential for use as biological monitors. Lichens may accumulate very high levels of Cd. *Cladonia alpestris* was sampled as an indicator of Cd pollution from a recently constructed Zn refinery in Finland. Jaakkola et al. (1971)

determined the background level of Cd was 0.1-0.2 ppm dry weight. They reported that after only 6 months operation of the zinc works, these lichens contained 1.0 ppm or a five-fold increase. Lichens are important potential biological monitors for atmospheric pollution especially in temperate or arctic areas.

Marine macroalgae have been used in measuring environmental gradients of Cd and as indicators of pollution. The most commonly used are *Fucus vesiculosus*, *Fucus serratus*, and *Laminaria digitata*, and also *Ascophyllum nodosum*, *Fucus spiralis*, *Chorda filum*, *Enteromorpha sp*., *Ulva lactuca*. Marine alga accumulate up to 220 ppm but normally <10 ppm dry weight of Cd.

In summary, certain mammal and bird species, earthworms and various higher plants especially food crop species, selected tree species, and certain lichens and algae have potential for monitoring Cd in terrestrial areas. In marine areas combined use of bivalve molluscs and macroalgae would appear to be highly effective. Use of marine and freshwater fish needs more study but appears to have more limited potential. Freshwater molluscs appear promising for monitoring Cd in streams and bodies of fresh water.

Chromium

Chromium accumulation has been fairly well studied in biological organisms and 627 species including 320 species of animals and 307 species of plants have been measured (Table 32).

Analysis of chromium is difficult and accurate methods have been available relatively recently. The compilation of Cr in organisms does not include many early analyses. Since these older data are suspect, they are not used in evaluating the results nor for selecting potential biological monitors.

There does not appear to be any biomagnification of chromium in higher trophic level predators.

Mammals

Mammals do not accumulate Cr to any great extent except in the hair and pelt. Concentrations of Cr in hair of ungulate herbivores and rodents may be very high. These mammals could be considered for selection as biological monitors. Hair and pelt of the cotton rat *Sigmodon hispidus* was used successfully to measure an environmental gradient of Cr used as a corrosion inhibitor in cooling water of a power plant. Contaminated mist was disseminated from the cooling tower (Table 15).

Birds

There are insufficient data on chromium in birds and the available information does not indicate capability of birds to accumulate Cr. No species are presently recommended for biological monitoring.

TABLE 32. SUMMARY OF CHROMIUM LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	25	D (0.0-5.0)	640.0	hair, heart, kidney	results variable
Birds	14	D (0.05-1.0)	D 1.0	----	need more data
Marine fish	92	D (0.1-5.0)	D 15.0	muscle, skin	need more data
Freshwater fish	38	W (0.0-0.5)	W 1.6	muscle	need more data
Molluscs	56	D (0.0-10.0)	D 145.0	soft parts	variable data
Crustacea	31	(0.0-5.0)	D 35.2	soft parts	variable data
Insects	2	----	D 1,500.0	----	need more data
Echinoderms	18	D (0.02-10.0?)	W 43.2	----	variable, need more data
Lower animals	42	D (0.0-10.0?)	D 75.3	----	variable, need more data
Higher plants	199	D (0.0-5.0)	D 500.0 A 30,000	leaf, twig	good bio-indicator
Mosses	11	D (0.5-15.0)	D 12,000	whole	good bio-indicator
Lichens	11	A (6.0-150.0?)	A 10,000	whole	good bio-indicator
Fungi	10	D (0.04-3.0)	----	whole	need more data
Algae	78	D (0.4-12.0)	D 110.0	whole	data variable
Total	627				

D = dry weight, W = wet weight, in ppm

Fish

Marine fish do not appear to be good biomonitors. Studies of levels of Cr in species of fish at ocean sewage dumps and sewage and industrial outfalls did not show fish to be suitable for monitoring environmental gradients of Cr. The dover sole was used to measure Cr gradient from a sewage outfall but the results were barely significant, especially since the Cr levels were so low that they approached the analytical method threshold. Over 92 species of marine fish have been analyzed for Cr concentrations and some show fairly high levels, but none are presently recommended for biological monitoring of Cr.

Freshwater fish have not shown any capability for use for measuring environmental gradients of Cr, and they do not accumulate high levels. Higher level predatory fish have relatively low levels of Cr. Isolated high concentrations of Cr in *Notropis* and *Percopsis* by Lucas et al. (1970) are based on single measurements and are excluded from consideration.

Molluscs

The data on accumulation of chromium in molluscs, while highly variable, show that molluscs can accumulate high levels and may have potential for biological monitoring. *Buccinum undatum* and *Patella vulgata* have been used to measure environmental gradients from an ocean sewage dump and a sewage outfall. Clams, mussels, oysters, limpets, scallops and periwinkles show capability of accumulating Cr. There is, however, a problem of highly variable data with high levels of Cr not known to be correlated with high environmental levels. More data especially on complicating factors such as season, age, size and temperature are needed.

Crustacea

The data on chromium concentrations in crustacea are similar to molluscs. Crustacea can accumulate high levels but the data are variable in regard to Cr levels in the environment. Three species have been used to measure environmental gradients of Cr, but the differences between source and control are not great, and data for *Acartia* may not be valid since they are based on measurements in two regions by different authors. Use of a crab for measuring an environmental gradient of Cr was statistically significant. Due to the variability of data no crustacea are presently recommended for selection as biological monitors of Cr.

Echinoderms and Lower Animals

The echinoderms and lower animals also show highly variable data and no species are known to have been used effectively for measuring environmental gradients of Cr. Annelid worms appear to be bioaccumulators of Cr and of the dozen species measured, all show high levels. This includes marine, freshwater, and terrestrial species. Annelid worms appear to have promise for biological monitoring, but more data are needed especially in monitoring environmental gradients of Cr.

Higher Plants

Higher plants effectively accumulate Cr and many species could be recommended for use in biological monitoring. Seven species were selected to show effectiveness in measuring environmental gradients of Cr (Table 15). The sources include a phosphate processing plant, gold mine and smelter, industrial, coal and oil combustion emissions, and serpentine areas. For many species it appears that there is no mechanism regulating or preventing accumulation of Cr; levels up to 500.0 ppm dry weight and 30,000 ppm ash weight have been recorded.

Some of the genera with potential as biological monitors of Cr based on high Cr accumulations are: *Agrostis*, *Armeria*, *Artemisia*, *Asplenium*, *Calamagrostis*, *Colluma*, *Cassinia*, *Dicoma*, *Dracophyllum*, *Empetrum*, *Festuca*, *Gentiana*, *Hebe*, *Hymenanthera*, *Lastrea*, *Leptospermum*, *Myosotis*, *Myrsine*, *Notothlaspi*, *Phormium*, *Pimelia*, *Plantago*, *Polypodium*, *Sagina*, *Sedum*, *Silene*, *Stellaria*, *Sutera*, *Thymus*, *Tillandsia* and *Viscaria*. Many of these species are localized, e.g. to New Zealand, and some are strictly serpentine species so that they would not be finally selected in comparison with widespread common species that occur in various ecological habitats.

Lower Plants

Mosses and lichens are excellent biomonitors of Cr and have been used effectively in biological monitoring of environmental gradients of Cr both in distances from sources and in time. The species of mosses to be considered include the genera *Dicranoweisia*, *Hylocomium*, *Hypnum* and *Sphagnum*. The lichens include *Hypogymnia*, *Lecanora*, *Parmelia* and *Peltigera*. There are insufficient data on fungi to consider selection of potential monitors. Marine algae bioaccumulate chromium in fairly high concentrations and have some potential for biological monitoring. However, the data are variable and no effective monitoring of environmental gradients of Cr was found. While Cr levels of 78 species of algae have been compiled there is presently little basis for selection of specific kinds of algae for use in biological monitoring. Data are needed on correlation of Cr levels in algae with environmental levels.

Cobalt

There have been 486 species of organisms analyzed for levels of Co including 251 species of animals and 235 species of plants (Table 33). There is relatively no biomagnification of Co in mammals and birds, and in some studies there appears to be an inverse relationship. However some predatory freshwater fish such as northern pike, muskellunge and walleye have accumulated fairly high levels of Co, but some bass did not. Molluscs, crustacea, and other lower animals can accumulate high levels of Co, the same as higher plants and algae.

Mammals and Birds

The limited available data for mammals and birds do not indicate that these organisms have value for potential biological monitoring organisms for cobalt.

TABLE 33. SUMMARY OF COBALT LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	15	W (0.0-0.3)	W <2.98	liver, kidney	
Birds	9	W (0.0-0.2)	----	liver	data sparse
Marine fish	63	W (0.0-0.2)	W 7.1	viscera, skin	data sparse
Freshwater fish	31	W (0.0-0.3)	W 13.0	liver, muscle	data sparse
Molluscs	62	W (0.0-1.0)	D 12.0	soft parts	data sparse
Crustacea	20	W (0.0-0.2)	D 14.3	----	data sparse and variable
Insects	3	----	----	----	data sparse and variable
Lower animals	48	D (0.0-2.0)	D 105.0	----	data sparse and variable
Higher plants	182	D (0.0-2.0)	A 17,700	leaf, twig	good indicators
Algae	53	D (0.0-2.0)	D 40.0	----	----
Total	486				

D = dry weight, W = wet weight, in ppm

Fish

Both marine and freshwater fish concentrations of Co show variable levels that cannot be explained by presence or absence of pollution. Even with elimination of earlier data using colorimetric methods of analysis, the remaining data are still variable, so that it is presently not possible to select any species of fish for potential biological monitoring of Co.

Molluscs

Of the 62 species of molluscs measured, some species accumulate large quantities of Co, probably as a result of Co apparently associating quickly with particulate matter and sediments thereby becoming unavailable for direct accumulation by other types of organisms. Stenoteuthis squid livers showed high levels of accumulation of Co^{60} in relation to a nuclear test, but other data on squid livers showed relatively low levels. The most promising mollusc for biological monitoring of Co appears to be Mytilus edulis.

Anthropods

The available data for crustacea are quite variable and no species appear suitable for biological monitoring based on present information.

Lower Animals

Both marine and freshwater annelid worms and corals appear to accumulate Co. However, the earlier data on marine worms may be questionable. Some species of coral have high levels of Co (to 105.0 ppm dry weight) and may be considered for biological monitoring.

Higher Plants

Some of the 182 species of plants measured for Co content accumulate very high concentrations of Co (to 17,700 ppm ash weight) and are excellent bioindicators for biogeochemical prospecting for Co deposits. Eight species have been used for measuring environmental gradients of cobalt. Some of the genera which could be considered for biological monitoring include Calamagrostis, Clethra, Comptonia, Crotalaria, Deschampsia, Linosyris, Nyssa, Pulsatilla, Rosa, Silene, Tillandsia and Vaccinium.

Lower Plants

Unfortunately no data were available on the levels of Co in mosses and lichens but this should be studied. Some marine algae such as Fucus and Ulva can accumulate high levels of Co and might be considered for marine biological monitoring.

In summary, molluscs, especially Mytilus edulis, annelid worms and corals appear to have value as potential monitoring animals for cobalt.

There are many species of higher plants that have been used effectively for biogeochemical prospecting and some for measuring environmental gradients of Co. Some of these and the marine algae Fucus and Ulva appear most promising for monitoring organisms for cobalt.

Copper

Copper concentrations in plants and animals have been well studied and data have been compiled on 885 species including 542 species of animals and 343 species of plants (Table 34). There have also been 54 studies on use of organisms for monitoring environmental gradients of Cu (Table 17).

Copper can become abundant in certain impact areas and habitats and may endanger various aquatic plants and animals, but it rarely poses a serious threat to human beings. Cu may be accumulated by oysters to such a degree

TABLE 34. SUMMARY OF COPPER LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	15	D (0.1-15.0)	D 93.0	liver, kidney, hair	
Birds	37	D (0.1-15.0)	D 367.0	liver, kidney, feathers	
Reptiles	1	----	W 15.0	egg	data sparse
Amphibia	4	----	W 318.9	liver	data sparse
Marine fish	143	W (0.0-10.0)	W 142.0	liver, gill	
Freshwater fish	40	W (0.1-10.0)	W 36.0	liver	
Molluscs	144	D (0.1-50.0)	D 15,160.0	liver	good accumulator
			W 3,300.0	digestive gland	data variable
Crustacea	71	W (0.1-30.0)	D 14,300	hepato-pancreas	data variable
Insects	21	D (6.0-20.0)	D 130.0	----	data variable
Lower animals	58	D (0.0-30.0)	D 149.9	----	data variable
Higher plants	235	D (1.0-20.0)	D 13,700		
Mosses	8	D (5.0-10.0)	D 1,340.0	----	
Lichens	17	D (7.0-15.0)	D 145.0	----	
Fungi	15	----	D 165.0	----	data sparse
Algae	76	D (1.0-25.0)	W 1,330.0	----	
Total	885				

D = dry weight, W = wet weight, in ppm

that they turn green and have a bitter copper taste. There appears to be a greater need for monitoring aquatic than terrestrial habitats, but effective monitoring organisms are available for either.

Mammals, Birds, Reptiles and Amphibians

Mammals bioaccumulate fairly high levels of Cu in the liver, kidney and hair. Birds accumulate Cu in liver, kidney and feather tissue, and amphibians in the liver. No species of mammals or birds or amphibia appear suitable for biological monitoring since none have shown correlations with environmental gradients of Cu and also since there is great variability of levels of Cu.

Fish

Data on concentration of copper have been compiled for 143 species of marine fish and 40 species of freshwater fish. No species have been used successfully for monitoring environmental gradients of Cu. The liver and vertebrae appear to have the highest concentrations. No species of fish are presently recommended for biological monitoring of copper.

Molluscs

Copper accumulation has been measured in 144 species of molluscs and 14 studies have shown the effectiveness of using molluscs for monitoring environmental gradients of Cu.

Bivalve feeders accumulate or bioconcentrate the highest levels of Cu, and oysters are well known for their ability to concentrate Cu ("greening"). In a study in Chesapeake Bay, *Crassostrea virginica* was used to measure the concentrations of Cu in the environment and maps were drawn with isolines showing the levels of copper (Bender et al. 1972).

The hepatopancreas and digestive glands concentrate the highest levels of Cu but it is also found in all of the soft parts, as well as in the shell. The digestive gland is the most promising tissue for analysis.

Oysters of the genus *Crassostrea* and mussels *Mytilus* and the limpet *Patella vulgata* appear to be excellent monitors of Cu. There are also data available on effect of various variable factors such as time of year, size and age, temperatures, depth of water and other factors affecting the level of Cu. The net uptake of Cu by *Mytilus edulis* has been shown to be affected by the presence and change in concentration of zinc, cadmium and lead. This is an important variable since it cannot be eliminated by the use of any particular sampling regime. This has led Phillips (1977) to suggest that *Mytilus edulis* should not be used as an indicator of copper pollution. It appears that other bivalves may be different in this respect (Roosenburg 1969) and accumulate much higher levels of Cu.

Certain molluscs have the potential of being the best biological monitors of Cu in the aquatic environment and *Busycon*, *Crassostrea*, and perhaps *Ostrea* and *Patella* are recommended for biological monitoring organisms for Cu. More study is needed for *Mytilus edulis*.

Crustacea and Insects

Crustacea can accumulate quite high levels of copper and 71 species have been studied. Five studies using crustacea for monitoring environmental gradients of Cu have been conducted.

Copper levels are highest in the hepatopancreas and the digestive gland, and it is found throughout the soft parts and muscle as well as in the exoskeleton or carapace. The Cu is stored in the hapatopancreas in the form of granules according to Djangmah (1970).

Certain species of barnacles, crabs, lobsters and shrimp would be suitable biological monitors for marine environments and crayfish and isopods for freshwater or terrestrial environments.

Some insects can accumulate copper but there are insufficient data to recommend any biological monitors.

Lower Invertebrates

Many of the lower invertebrates accumulate fairly high levels, but only the echinoderms *Arbacia lixula* and *Paracentrotus lividus* have been used successfully to measure environmental gradients of Cu (Sheppard and Bellamy 1974). Certain annelid worms have high levels and appear to deserve more study with regard to their suitability for monitoring Cu.

The only species of lower invertebrates presently recommended for monitoring Cu are the echinoderms *Arbacia* and *Paracentrotus*; however, the limited data and range of distribution limits their potential value.

Higher Plants

Copper has been analyzed in 235 species of higher plants and many accumulate Cu in high concentrations. Sixteen species have been used effectively to measure environmental gradients of Cu (Table 18) from various sources such as different smelters, urban and industrial air pollution, sewage sludge, mine effluent and a contaminated bay.

Many species of plants appear to absorb and accumulate Cu without limitation or regulation, especially "hyperaccumulators" such as the copper plant *Aeolanthus biformifolius* (Mailaise et al. 1978) which grows in copper rich soil in Zaire. Various plants are effective economic indicators of Cu and are used in biogeochemical prospecting. Some species are "Primary indicator plants" that occur only where Cu occurs in quantity. Levels up to 13,700 ppm dry weight of copper have been found in plants. Copper is found in all of the plant tissue and may be highest in the root or corm, but also occurs in the leaf, shoot and stem or twig.

A variety of species have excellent potential for biological monitoring of Cu. These include aquatic species such as *Anacharis*, *Nuphar*, *Potomogeton* and *Equisetum* in freshwater habitats, and *Zostera* in marine and brackish water. There are also various grasses such as *Deschampsia*, *Festuca* and *Panicum*, the shrubs Comptonia and Vaccinum and trees such as Betula, Pinus and Populus. Various economic indicators of copper also deserve consideration for biological monitoring.

Mosses, Lichens and Fungi

Seven species of mosses and lichens have been used to measure environmental gradients of Cu air pollution and fallout from smelters, copper mine area, steelworks and metallurgic industry. The moss Hypnum cupressiforme has been used to monitor levels over geographic areas, and changes in level of Cu with time from 1870 to 1969. It has also been used effectively in measuring gradients using transplants. One moss Meirlichhoferia macrocarpon is known as "copper moss" because of the high levels of Cu accumulated.

Mosses and lichens are highly recommended for monitoring Cu. The most promising genera appear to be Dicranoweisia, Hylocomium, Hypnum, Pleurozium, and perhaps Spagnum. The most promising lichens presently known are Hypogymnia, Lecanora, Parmelia and Peltigera.

Fungi can accumulate high levels of Cu but the data are variable and presently there is insufficient information to select monitoring organisms.

Algae

Copper as copper sulfate is an effective algicide for freshwater algae and is used extensively for control. Marine algae accumulate Cu and 76 species have been analyzed with a recorded maximum of 301.0 ppm dry weight. Marine algae of the genera Ascophyllum, Enteromorpha and Fucus have been used effectively for monitoring environmental gradients of Cu from effluents from metal smelters, and a desalination plant. The toxic effects of Cu on algae must be considered. Bryan (1969) suggested that the toxic effects of Cu possibly promoted its own entry into Laminaria digitata. Seasonal variation in concentrations of Cu in algae has been reported for some species of macroalgae but in Fucus vesiculosus Bryan and Hummerstone (1973) found little seasonal variation.

The most promising macroalgae for monitoring Cu appear to be Ascophyllum, Enteromorpha, Fucus, Ulva and perhaps Sargassum.

Lead

There is an abundance of carefully documented data on levels of lead in biological organisms. Over 951 species of plants and animals have been measured including 626 species of animals and 325 species of plants (Table 35). Review of these data plus 95 examples of use of organisms for monitoring environmental gradients of Pb permit a wide selection of organisms for monitoring (Tables 19 and 20).

Lead is of major importance as a toxic trace metal that contaminates man, his food, plants and animals and his environment. Lead constitutes a real threat to various human populations especially young inner-city children. It is therefore essential to select biological monitoring organisms that will

TABLE 35. SUMMARY OF LEAD LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	55	W (1.0-10.0)	W 549.0	bone, kidney, liver, hair	good indicator
Birds	61	W (1.0-10.0)	350.0	bone, kidney, liver	good indicator
Reptiles	2	----	0.5	egg	data sparse
Amphibia	3	W (0.5-5.0)	D 7,329.0	gut, bone	data sparse
Marine fish	140	D (0.0-5.0)	D 50.0	gill, skin	not good indicator
Freshwater fish	90	D (0.0-5.0)	D 814.0	"gut"	not good indicator
Molluscs	118	D (0.0-15.0)	D 3,100.0	soft parts	good accumulators
Crustacea	55	D (1.0-20.0)	D 500.0		good accumulators
Insects	41	----	D 14,233	whole	data sparse and variable
Echinoderms	6	D (1.0-20.0)	D 460.0	soft parts	good Pb accumulators
Annelids	24	D (1.0-30.0)	D 624.0	whole	good Pb accumulators
Coelenterates	22	D (0.4-4.0)	W 130.0	whole	data sparse and variable
Tunicates	4	----	D 14.5	whole	data sparse and variable
Lower animals	5	----	D 68.0	whole	data sparse and variable

(continued)

TABLE 35. (Continued)

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Higher plants	184	D (1.0-10.0)	D 11,750	whole	excellent indicators
Mosses	49	D (1.0-30.0?)	D 16,670	whole	excellent bioindicators
Lichens	23	----	D 12,045	whole	excellent bioindicators data variable
Fungi	1	----	----	----	data sparse
Algae	68	D (1.0-10.0)	W 14,190	whole	data variable
Total	951				

D = dry weight, W = wet weight, in ppm

measure the critical immediate environment of man, critical pathways and critical sources of lead as well as the global environments and trends with time.

Mammals

Fifty-five species of mammals have been measured for levels of lead. These include species closely associated with man, such as the dog, cat, rat, horse, cow and house mouse and all of the important domestic animals for food. Also a variety of small rodents and larger herbivorous ungulates have been studied. Hair, bone, kidney, and liver tissues have the highest levels of Pb, but milk, blood and the whole animal have been used for measuring gradients of Pb.

With a large number of potential monitoring organisms available, final selection can be based on factors such as association with man, geographic distribution, cost, convenience, and especially the specific ecological areas or habitats to be monitored.

Birds

Sixty-one species of birds have been measured for lead levels. These include pigeons, English sparrows, starlings and robins often associated with man. Also chickens, turkeys, ducks and pheasant, which serve as food, have been measured. Seven species have been used for measuring environmental gradients of lead. The tissues which have the highest levels of lead include bone, especially the femur, and kidney and liver tissue. In addition, eggs, egg shells, and feathers have been used successfully for measuring levels of Pb.

There are many species of birds which can be used for biological monitoring of Pb and final selection will be based on monitoring needs, the same as for mammals.

Amphibia and Reptiles

Amphibia accumulate high levels of lead, and the gut, bone, and kidney tissue appear to have highest levels. While the data for frogs and toads are limited, they deserve more study and consideration for use for biological monitoring.

Fish

While 250 species of fish have been measured for concentrations of lead, only a few have been marginally suitable for measuring environmental gradients of lead. In general, fish do not accumulate high levels of lead except in special circumstances and there are no good correlations with environmental levels. Only one species of marine fish used in monitoring gradients of Pb could be considered. Results of other studies were not statistically valid. A few species of freshwater fish in heavily polluted areas showed somewhat higher levels of Pb than in controls, but none of these are recommended for biological monitoring. There is evidence that biominification occurs in fish. Higher trophic level predators have lower levels of Pb than prey. The gut of the bluegill in a heavily polluted Pb tailings pond had the highest level of any fish. The tissues with the highest level include the gut, gill and skin.

Molluscs

Lead concentrations have been studied in 118 species of molluscs and five species have been used successfully to monitor environmental gradients (Table 19). Some molluscs accumulate very high levels of lead and appear to be potentially excellent biological monitoring organisms. However, the feeding habits of various molluscs are very different and species must be picked carefully. Members of the genus *Mytilus* appear attractive but they take up sediments and may reflect sedimentary levels instead of levels of lead in the aquatic environment. Further, molluscs do not always correlate with known pollution. The limpet *Acmaea digitalis* had 931.0 ppm of Pb dry weight in an area near high vehicular traffic, but only 7.5 ppm dry weight near heavy sewage pollution and some traffic. This species lives and feeds from rock surfaces not thoroughly rinsed by high tides (Graham 1972). This illustrates an example of the care that must be taken in selecting mollusc species for monitoring. Also some species were not successful in monitoring environmental gradients of Pb.

Certain molluscs and especially *Mytilus* appear to have potential for specific types of biological monitoring of lead. This will be discussed in more detail under final selection of monitoring organisms. Nearly all tissues including the shell contain Pb.

Crustacea

Crustacea accumulate high levels of lead, and of the 55 species studied, several have promise for monitoring. In freshwater, crayfish accumulate high levels and indicate levels of Pb present. In the marine environment, some of the groups to be considered include *Carcinus*, *Cragon*, *Palaemonetes* and perhaps some copepods.

Many of the crustaceans such as crabs are scavengers and would be expected to accumulate Pb. The exoskeleton, digestive gland, gills and muscle usually have higher levels of Pb.

Insects

Both aquatic and terrestrial insects can accumulate high levels of lead. Available data for 41 species are rather variable and few studies have shown capability of insects to measure environmental gradients of lead. Fruit flies *Drosophila* have been used by Lower (1974) to measure environmental levels of lead from smelters. There was agreement between high levels at sources and lower levels at distances but with unexplained sudden increases between. *Drosophila* are nearly worldwide in distribution and need to be tested more. Some aquatic larvae and nymphs of various groups of insects have high levels in polluted areas and deserve consideration for biological monitoring. Various groups of predatory, sucking and chewing insects were effective in measuring environmental gradients of lead from a highway (Illinois 1974).

Echinoderms

All of the lead levels measured in echinoderms are high. Two species of sea urchins were effective in monitoring Pb in the polluted Bay of Naples in comparison with controls. *Arbacia* and *Paracentrotus* appear to have promise for biological monitoring of lead.

Annelids

Earthworms accumulate lead and show good capability in monitoring environmental gradients of Pb. They are widespread in temperate areas and have promise for biological monitoring. Freshwater tubificid worms grow in heavily polluted areas and should be studied further. There are insufficient data on marine annelids to make recommendations.

Coelenterates, Tunicates and Other Lower Animals

A number of species of coral have been studied but there is little evidence of their ability to monitor environmental levels of lead. The data are sparse and variable for all coelenterates, tunicates and other lower animals. None of these species are recommended for biological monitoring.

Higher Plants

Higher plants accumulate Pb from uptake from the soil and from the air. In addition, they may be externally contaminated by surficial deposition of Pb. They are excellent biomonitors and have been used extensively to measure environmental gradients of Pb. A large number of species of plants have been used to monitor gradients of Pb from highways and some of these have been quoted. To give a wider scope to monitoring use, 33 species have been selected to present results from various types of sources and gradients (Table 20). There are ample data on lead levels in cultivated crops, shade trees and other plants closely associated with human habitation. There are sufficient data on many species suitable for monitoring so that final selection can be made based on other factors of importance in biological monitoring.

Mosses and Lichens

Mosses and lichens have been used extensively to measure environmental gradients of Pb, changes of concentration over periods of time, and to measure and map pollution isolines. An elegant method of using moss bags for measuring deposition of lead per time period has been developed by Goodman and Roberts (1971) and Little and Martin (1974). Various species of mosses and lichens are highly recommended for biological monitoring especially the mosses *Hylocomium*, *Hypnum*, *Pleurozium* and *Sphagnum* and the lichens *Cladonia*, *Lecanora*, *Parmelia* and *Peltigera*.

Algae

Certain freshwater species of algae including *Cladophora* and a few marine species such as *Ascophyllum* and *Fucus* have been used to measure environmental gradients of lead. While there have been 68 species of algae analyzed for lead content, there are few critical studies on use of algae for measuring environmental gradients of Pb. Marine algae can measure the amount of Pb in solution in the seawater, but more critical studies are needed. *Cladophora* and other freshwater algae, and the marine algae *Ascophyllum*, *Fucus* and perhaps *Enteromorpha* and *Ulva* can be recommended for biological monitoring of lead.

Mercury

Mercury is bioaccumulated to fairly high concentrations in nearly all groups of animals. Bioaccumulation in plants is uncommon and only to relatively low levels. Filter feeding organisms especially molluscs and scavenger type animals may accumulate high levels of Hg.

Mercury has been studied extensively in biological organisms and data have been compiled for 1,076 species. The available literature is so extensive that an exhaustive compilation might have doubled this list. However, for the purpose of determining the best biological monitoring organisms the data selected appear adequate. Animal studies include 872 species and the analyses of Hg in plants includes 204 species (Table 36).

TABLE 36. SUMMARY OF MERCURY LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Marine mammals	26	W (0.01-10.0)	W 765.0	liver, hair	high levels Hg
Mammals	71	W (0.01-2.0)	W 392.0	fur, liver	high levels Hg
Water birds	87	W (0.01-3.0)	W 175.0	liver, feathers	high levels Hg
Birds of prey	33	W (0.01-5.0)	W 270.0	liver, feathers	high levels Hg
Terrestrial birds	52	W (0.01-3.0)	W 140.0	liver, feathers	high levels Hg
Reptiles	2	----	W 0.71	----	
Amphibia	12	W (0.03-2.0)	W 25.9	liver, kidney	
Marine fish	261	W (0.01-2.0)	D 309.1	liver, kidney	
Freshwater fish	111	W (0.01-2.0)	W 52.0	liver, kidney	good monitors
Molluscs	77	W (0.01-2.0)	D 181.0	ganglion, soft parts	good monitors
Crustacea	66	W (0.01-2.0)	D 100.0	muscle, soft parts	
Insects	52	W (0.01-1.0)	W 17.0	whole	
Lower invertebrates	22	W (0.0-1.0)	D 56.0	whole	
Higher plants	106	W (0.0-0.2)	W 59.0	leaf	fairly poor monitoring organisms
Mosses	18	W (0.03-0.3)	W 3.7	whole	fairly poor monitoring organisms
Lichens	10	(0.0-0.3)	D 0.999	whole	fairly poor monitoring organism

(continued)

TABLE 36. (Continued)

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Fungi	21	W (0.0-0.2)	D 47.1	whole	fairly poor monitoring organism
Algae	49	D (0.02-0.5)	D 25.537	whole	
Total	1,076				

D = dry weight, W = wet weight, in ppm

Sufficient studies of Hg concentrations in organisms have been made to permit selection of animal and plant species in various types of habitats including urban, rural, aquatic freshwater and marine and diverse ecological types of terrestrial areas.

Mammals

Marine mammals have been well studied and 26 species have been measured for levels of Hg. Various species of seals, dolphins, porpoises, whales, and sea lions have accumulated very high levels of Hg in the liver, kidney and hair. The maximum level was 765.0 ppm wet weight in liver of a harbor seal found dead in the Netherlands (Koeman et al. 1971). However, about 200 ppm dry weight is not unusual and 1,547.0 ppm dry weight was found in a harbor seal in West Scotland (Hamilton 1976). There are large variations in the concentrations of Hg in marine mammals; one of the reasons for the variation is probably age. Some of the species are highly migratory. There does not appear to be a correlation with geographic area except that there are more records of high levels of Hg on the west coast of the United States and around Europe, but high levels also occur in more remote places. The ringed seal _Phoca hispida saimensis_ was used to monitor an environmental gradient of Hg by Häsänen (1974).

Over 71 species of terrestrial mammals have been analyzed for Hg levels and many of them have high concentrations. Various small rodents accumulate Hg and two species have been used to measure environmental gradients of Hg. Some of the animals associated with man which would be suitable for monitoring are the cat, rat and pig. Cats have been used to monitor mercury pollution in Japan and in Canada (Takeuchi et al. 1977). Hair samples of cats would be excellent tissue for monitoring. Rat or pig hair, liver or kidney tissue could be used. Mammals appear promising for monitoring Hg.

Birds

Since there are rather extensive data on Hg in 172 species of birds, they have been divided into three groups: water birds, birds of prey, and terrestrial birds.

The water birds showing accumulation of Hg include ducks, herons, gulls, mergansers, cormorants, grebes, terns and others. Some of the fish-eating and scavenger-type aquatic birds show high levels of Hg and could be considered for biological monitoring.

Birds of prey often have high levels of Hg, but many of these predators are relatively uncommon or rare and are decreasing in abundance from various pollutants including mercury. For practical purposes, no birds of prey are included as potential monitoring organisms but predatory birds found dead and unhatched eggs should be measured for Hg.

Fifty-two species of terrestrial birds have been studied for levels of Hg and many show fairly high levels, especially if they have fed on seed grain treated with mercury to prevent fungal diseases. Some of the species which could be used for monitoring include the pigeon and pheasant. Scavenger birds also show ability to accumulate high levels of Hg, and crows, hooded crows, ravens and magpies would appear to be suitable for monitoring. Starlings also show high levels of Hg in the liver and kidney.

Reptiles and Amphibia

There are insufficient data on reptiles to consider any species for monitoring organisms.

Amphibia appear to have promise for biological monitoring of Hg. They are predacious as adults and some species of toads and frogs show high levels of Hg in the liver and kidneys when they are in areas with high environmental levels of mercury. *Bufo bufo* and *Rana temporaria* occurring in an Hg mining area showed high levels of Hg in comparison with controls. Amphibia deserve to be studied more with regard to accumulation of Hg and other toxic metals. Some frogs and toads could be considered for biological monitoring of Hg.

Fish

Data have been compiled on mercury levels in 251 species of marine fish, and many more species have been studied. However, only two species are known to have been used successfully for measuring environmental gradients of Hg. The English sole *Parophrys vetulus* and the sand sole *Psettichthys melanosticus* were used to measure gradients from a chloralkali plant. Other studies have given negative or statistically non-significant data. Except for ocean dumps, outfalls, and some industrial wastes along coasts there are not many high environmental marine concentrations of mercury in comparison with freshwater. The high levels of Hg in higher level predators such as swordfish, tuna, marlin and sharks is derived from accumulation with age and from biomagnification resulting from usually natural levels of Hg in the ocean and not from pollution by man. Analyses of tuna preserved for about 100 years confirm the fact that tuna have natural high levels not due to pollution by man. Some species of marine fish exposed to high levels of mercury pollution from a chloralkali plant in Minamata Bay, Japan, had very high levels which contributed to the outbreak of mercury poisoning called Minamata disease.

There is a long list of species of fish and an enormous mass of data on Hg levels including data on levels in different tissues, size and age of fish, and geographical areas. Various species could be selected for monitoring depending on the desired objectives of monitoring. It would appear that monitoring large predators such as tuna, swordfish, marlin and other similar types would be of little value for environmental monitoring, but only of value in relation to human consumption of the muscle. Monitoring of wide ranging or migratory species would also not appear to be of value. If it is desired to monitor polluted shores, bays, harbors or around sewage and industrial outfalls and dumps, there are a number of species available including English and sand sole, flounder and other bottom-feeding fish, and other species typical of these areas. Local predators such as certain smaller sharks might be studied for suitability for monitoring.

Freshwater fish have been studied in great detail. Data have been compiled on 111 species; however, there is a very large literature including additional species of freshwater fish and much confirmatory and duplicating information. Many countries and most of the states of the United States have conducted extensive studies on levels of Hg in fish used for human consumption, and also for checking the amount of pollution from municipal and industrial waste. Thirteen studies using ten species of freshwater fish have been conducted on monitoring environmental gradients of Hg. The pike _Esox lucius_ is a widespread predator which has been studied extensively and much is known on levels in the various tissues with age, size, time of year, rate of uptake and loss, and other factors. This would appear to be the best freshwater species of fish for biological monitoring. Other species such as brown trout, bass, perch, salmon and walleye might be considered.

Molluscs

Seventy-seven species of molluscs have been analyzed for mercury content and five species have been used to measure environmental gradients of Hg. Molluscs can accumulate fairly high levels of Hg in polluted areas. Filter feeding molluscs accumulate Hg from food, from solution and also by ingestion of inorganic and organic particulate matter. Bivalve molluscs therefore reflect the concentration of Hg primarily at the bottom of the water body where they occur. The research on the effects of different variables on use of bivalves as indicator surveys has been reviewed by Phillips (1977). The variables include organism, age, weight, size and sex, season, position of sampling, salinity, water temperature, and the coexistence of several metals. These have been studied with regard to the net uptake of the metals by bivalves and the final concentration of metals found in the organisms.

Bivalves used for monitoring Hg include _Anodonta grandis_, _Mya arenaria_, _Mytilus californianus_, and _Mytilus edulis_. The latter species is nearly worldwide in distribution and may be a very suitable species for biological monitoring. Some species of oysters Crassostrea and Ostrea show high accumulation levels of Hg and should be considered.

Crustacea

Crustacea include scavengers and predators. Some species accumulate fairly high levels of Hg especially certain decapod crustacea such as crabs, lobsters and crayfish. Freshwater crayfish appear most promising based on four examples of measuring environmental gradients of Hg. Decapod crustacea have been dismissed by Phillips (1977): "however, because of the rapid turnover of metals in these organisms, they do not appear to be useful indicators of trace metal pollution."

Crustacea in the Minamata Bay in Japan had very high levels of Hg. Certain crabs, crayfish and perhaps the sowbug Ascellus may be considered for biological monitoring organisms for Hg.

Insects

Fifty-two species of insects have been analyzed for Hg content. Various blowflies infesting Hg containing fish showed Hg accumulation. Some aquatic insects collected in the water below paper mills had high levels of Hg and were used effectively in measuring environmental gradients of Hg. No species of insects are presently recommended for biological monitoring of Hg.

Lower Invertebrates

Of the various types of lower invertebrates studied, only annelids appear to show promise for biological monitoring of Hg. Leeches and the earthworm Lumbricus terrestris were successfully used in monitoring environmental gradients of Hg and earthworms could be considered for biological monitoring.

Higher Plants

While 106 species of higher plants have been studied for Hg levels, they are generally not good accumulators of Hg with a few exceptions. Some species growing over cinnabar or grown in Hg-treated soil can absorb fairly high levels of Hg and some plants apparently accumulate mercury (e.g., on bark) from fallout from smelters and factories. Aquatic plants such as the water lily may accumulate Hg. Wild rose Rosa acicularis was used to monitor an environmental gradient of mercury from an Hg smelter, but the data comparing levels near the sources and a control at some distance were not statistically significant (O'Toole et al. 1971).

Since there is relatively low accumulation of Hg in higher plants, and problems with differentiating between external contamination and absorbed Hg, no species appear especially promising for monitoring Hg. There are, however, some species which are very good for biogeochemical prospecting for Hg. If needed, there are several higher plants such as Arenaria, Betula, Calamagrostis, Galium, Holostium, Prunus, Stellaria and others which could be considered.

Mosses, Lichens and Fungi

Mosses do not accumulate high levels, but three species have been used successfully to measure environmental gradients of Hg. Dicranum and Hylocomium were used to measure atmospheric fallout of Hg, and the aquatic moss Fontinalis were used to measure pollution in a river below a pulp paper mill. These could be considered for biological monitoring of Hg if needed.

Only a few species of lichens have been analyzed for levels of Hg and none show promise for biological monitoring of Hg.

Twenty-one species of fungi have been analyzed for Hg concentrations. Lactarius deliciosus was used successfully to monitor an environmental gradient of Hg from a smelter and could be considered for monitoring.

Algae

Marine algae analyzed for Hg levels include 49 species. A few species accumulate fairly high levels of Hg, but there was poor correlation with environmental levels or with sources except at Minamata Bay, Japan with Ulva pertusa. No species of marine algae are presently recommended for biological monitoring of Hg.

Nickel

Concentrations of nickel have been measured in 641 different species of biological organisms including 276 species of animals and 365 species of plants (Table 37).

Nickel levels are not increased as one ascends higher trophic levels of food chains nor do predatory animals have higher concentrations. These characteristics plus low absorption and rapid excretion and regulation by mammals and birds result in relatively low accumulation levels. The available data for molluscs, crustacea and other lower animals are highly variable.

Nickel is common, widely distributed, and is found in most organisms tested. It is also found to be concentrated in some areas containing Ni ores, serpentine soils, and polluted areas from man's activities. There are many examples of high concentration levels in organisms capable of accumulating Ni.

Mammals and Birds

No species of mammals appear to have potential as biological monitoring organisms. The highest level recorded was in a harbor seal.

No species of birds appear promising for monitoring nickel except perhaps the black-backed gull which is a scavenger and had 5.0 ppm dry weight in kidney tissue.

Fish

Marine and freshwater fish when exposed to Ni pollution show fairly high levels especially in the kidney, liver, skin and gill tissue. On the basis

TABLE 37. SUMMARY OF NICKEL LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	13	W (0.0-3.67)	W 9.0	kidney & liver	
Birds	12	W (<0.02-1.66)	W 4.96	kidney & liver	more data needed
Marine fish	80+	W (ND-4.0?)	D 163.9	kidney, skin	data variable
Freshwater fish	24	W (<0.2-?)	W 51.6	kidney	data variable
Molluscs	55	W (0.4-2.0)	W 191.0	soft parts	
Crustacea	25+	W (0.01-9.8)	W 39.0	whole	good indicator
Insects	5	----	D 5,000.0	----	maximum in termites
Echinoderms	12	----	W 78.0	skeleton	more data needed
Lower invertebrates	50	D (2.0-?)	W 57.0	----	data variable
Higher plants	239	D (2.0-15.0)	D 47,000	leaf	good indicator of Ni
Mosses	8	D (0.3-4.0)	D 900.0	plant	good indicator of Ni
Lichens	30	D (1.0-12.0)	D 420.0	plant	good indicator of Ni
Fungi	2	----	D 3.5	----	more data needed
Algae	86	D (0.2-15.0?)	W 1,070.0	plant	good indictor of Ni
Total	641				

D = dry weight, W = wet weight, in ppm

of available data, even though over 100 species of fish have been measured for Ni concentrations, it is difficult to select any species of fish for monitoring due to the high variability of data and lack of valid experience using fish for monitoring environmental gradients of Ni.

Molluscs

Molluscs may have very high levels of nickel, but the data are quite variable and high levels are often not correlated with high environmental levels of Ni. Three species have shown correlation with environmental gradients of Ni. Some authors have called attention to the problem of elimination of particles or grains in the tissue that can give unusually high readings. While more study and data are needed, it appears that *Buccinum*, *Placopecten* and perhaps *Pecten* and other species of molluscs could be considered for potential biological monitoring candidates for Ni.

Crustacea

Crustacea appear to have higher levels of Ni than any other group of animals. However, the levels are highly variable and do not appear to be correlated with environmental Ni, except species of crab, a prawn and a fresh-water crayfish which have been used effectively to measure environmental gradients of ni. Certain crustacea appear to have some promise for biological monitoring, but more research is needed to understand the variability and effects of various factors.

Echinoderms and Lower Animals

Many of the species of echinoderms and other lower animal groups have high levels of nickel, but as in crustacea and molluscs, the results are highly variable and not known to be correlated with high environmental levels of Ni. This needs to be investigated before using these organisms for biological monitoring. There appears to be some promise but the best potential monitoring species cannot be selected at present. Use of the echinoderm *Arbacia lixula* and earthworms for measuring environmental gradients of Ni gave non-statistically valid results for the echinoderm, and borderline results for the annelids. No lower animal species are presently recommended for monitoring Ni.

Higher Plants

Higher plants appear to be unable to regulate Ni accumulation and many accumulate or concentrate extremely high levels. There are numerous species that are excellent for use in biogeochemical prospecting for ores and some species have been used commercially for Ni prospecting. Many species fit the category of hyperaccumulator since they contain in excess of 1,000 ppm dry weight basis or 1 percent Ni in dry leaves (Brooks et al. 1977). In addition, 19 species of higher plants have been used effectively in monitoring environmental gradients of Ni. The number of plant species that could be used as potential biological monitoring species is so large that selection should be based on other characteristics such as widespread geographical distribution, ease of sampling, yearly variation in levels of Ni and capability for concurrently monitoring other toxic metals. Various species are available for monitoring aquatic as well as urban and various ecological types of areas.

Mosses, Lichens and Algae

All of these plants accumulate nickel readily, the same as higher plants, and have real potential for monitoring. Four species of mosses and five species of lichens have been used successfully for monitoring environmental gradients of Ni. Probably many more species are being used since this field of monitoring is receiving much attention at present. Transplanting mosses into polluted areas where they do not presently occur and use of moss bags are highly effective for monitoring atmospheric Ni. Many species of mosses and lichens are available for use as potential biological monitoring organisms, especially the species used extensively in the Fenno-scandian countries.

Marine algae accumulte high levels of Ni but none are known to have been used to monitor environmental gradients. Some species could be considered for biological monitoring of Ni.

Selenium

Selenium is accumulated by different types of organisms especially plants. A total of 298 species of organisms have been analyzed for Se content including 152 species of animals and 146 species of plants (Table 38).

Only nine species of organisms have been tested for ability to monitor environmental gradients of selenium (Table 24). One species of fish and the crab *Cancer anthonyi* showed negative correlation, and the jumping mouse *Zapus princeps* and spanish moss showed marginal results. Some species of higher plants appear to accumulate Se without limit and some indicator plants require presence of Se before they can grow.

Mammals and Birds

Many mammals accumulate large quantities of selenium in the hair which appears to be the best tissue to sample, but the kidney and liver also accumulate it. Predatory seal and sea lion accumulated very high levels of Se in the liver. Hair and claws should also be checked. Some rodents in seleniferous areas accumulated high levels of Se in the kidney and hair. The data on Se in birds are sparse but three species of marine birds had high levels in the liver. No species of mammal or birds are presently recommended for selection for biological monitoring of selenium.

Amphibia

While toad liver was used for measuring an environmental gradient, there are too few data to recommend any amphibia for biological monitoring of selenium.

TABLE 38. SUMMARY OF SELENIUM LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	35	W (0.02-2.0)	D 352.0	liver, hair, kidney	very high in seal and sea lion
Birds	8	W (0.01-4.0)	W 4.6	liver	data sparse
Amphibia	2	----	W 4.7	liver	data sparse
Marine fish	10	W (1.0-4.0?)	W 13.5	liver	data sparse
Freshwater fish	63	W (0.1-1.0)	W 6.0	whole	predators low Se
Mollusca	11	W (0.002-3.0)	W 3.9	soft parts	data sparse and variable
Crustacea	8	----	W 15.66	----	data sparse and variable
Insects and Arachnids	6	----	67.0	----	data sparse and variable
Echinoderms	7	----	D 4.4	----	data sparse and variable
Tunicates	2	----	D 5.1	----	data sparse and variable
Higher plants	118	W (0.0-0.3)*	D 14,929 A 40,000	leaf, stem and fruit	excellent indicators
Fungi	19	(0.13-3.0?)	D 7.02	spore, cap, and stalk	data sparse
Algae	9	----	W 2.2	----	data sparse
Total	298				

* in non-seleniferous areas, including plant data not cited from Schroeder et al. (1970).

- in seleniferous area data highly variable.

D = dry weight, W = wet weight, A = ash weight, in ppm

Fish

Some marine fish accumulate fairly high levels of Se but there are too few data available to select any biological monitors. Muscle tissue of the dover sole *Microstomus pacificus* was measured in a heavily polluted area compared with non-polluted, and the sole in the heavily polluted area had slightly less Se (Fowler et al. 1975). Similar results were observed by DeGoeij et al. (1974).

Freshwater fish appear to have much less Se than marine fish. Freshwater predators such as pike, muskellunge, bass (with one exception), sauger and walleye all had relatively low levels. Carp, some species of catfish and suckers which are scavenger type fish generally had higher levels of Se. No species of fish are presently recommended for biological monitoring of Se.

Molluscs, Crustacea and Insects

There are few data on levels of Se in molluscs, but some appear to accumulate it. More data are needed for species such as *Mytilus edulis*. Some crustacea accumulate Se but the data are sparse and variable. The crab *Cancer anthonyi* showed negative correlation with environmental gradient of Se. Some insects feeding on plants with high Se showed high levels. No species are recommended for biological monitoring, but *Mytilus edulis* might be considered.

Lower Animals

Some echinoderms and tunicate species accumulated fairly high levels of Se but there are insufficient data to select any species for biological monitoring. Earthworms along roadside in Vermont had 5.81 ppm wet weight of Se according to Schroeder et al. (1970), and should be studied in more detail for potential biological monitoring.

Higher Plants

Plant species have been categorized into several groups by Roosenfeld and Beath (1964). a) "Primary selenium indicators" -- accumulate high concentrations of Se when they grow on seleniferous soils or geological formations. They are primary Se indicators since their growth is restricted to seleniferous areas. These include about 24 species of the genus *Astragalus*, the section *Xylorhiza* of the genus *Machaeranthera*, the section *Oonopsis* of the genus *Haplopappus*, and *Stanleya*. These species require Se for their growth and development. b) "Secondary selenium absorbers" -- absorb moderately large quantities of Se when they grow on soils that contain high concentrations of available Se. These species include a number of plant genera such as *Aster*, *Atriplex* and *Grindelia*.

When cattle or other livestock eat these plants with high concentrations of Se they develop "blind staggers" or acute selenosis.

The above species of plants, especially the "secondary selenium absorbers" could be considered for biological monitoring of Se. Certain grasses including wheat also accumulate Se and could be convenient organisms for biological monitoring. A large number of species of plants from Vermont all had less than 1.0 ppm wet weight and are not included in Volume 2. However, leaves of trees growing in a remote forest in Vermont had the following Se concentrations (colorimetric method) spruce 7.79 ppm, oak 1.13 ppm, maple 1.44 ppm, poplar 3.25 ppm, wild apple 4.37 ppm, and basswood 11.38 ppm, all wet weight (Schroeder et al. 1970).

Fungi and Algae

There are insufficient data to recommend selection of any fungi or algae, for biological monitoring. Unfortunately no data on mosses and lichens were found on monitoring Se in the available literature.

Tin

For selecting the best monitoring organisms, the data on tin concentrations in 157 species of plants and animals were compiled, together with data on use of organisms for monitoring environmental gradients of Sn (Table 39).

Tin is not widespread, is only locally common, and it is not highly concentrated by animals as far as is known. There have been difficulties in making accurate quantitative measurements of Sn. Therefore the data are meager and older data are suspect and not used. While 71 species of animals have been measured for Sn, most data are too meager to effectively select species for monitoring.

Mammals and Birds

It is interesting that the heart of a beaver (7.28 ppm wet weight) and the liver of a fox (3.50 ppm wet weight) are high in Sn but the significance and perhaps validity need to be determined. No significant data on birds are available.

Fish

There are few data on the concentrations of tin in marine fish, but levels in muscle of codfish 3.67 ppm wet weight and 3.21 ppm wet weight in winter flounder might be of interest for monitoring, after further study. Freshwater fish have been better studied and fairly high levels have been found in carnivorous fish near the highest trophic levels. The northern pike, 5.43 ppm, and up to 17.0 ppm wet weight of tin by Uthe and Bligh (1971) and Tong et al. (1972) respectively, indicate that muscle tissue of pike may be of value for use in monitoring. Other predators such as smallmouth bass (to 6.0 ppm) and largemouth bass (to 6.0 ppm) and especially walleye (to 20.0 ppm) wet weight also indicate species of potential value for biological monitoring of tin.

Lower Animals

Most of the data on tin in lower animals is fairly old and the results are suspect until rechecked with recent more sophisticated and accurate measuring

TABLE 39. SUMMARY OF TIN LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	10	W (0.0012-1.5)	D 15.0	muscle, liver, adrenal	data sparse or not reliable
Birds	2	----	W 1.73	muscle	data sparse or not reliable
Marine fish	8	----	W 3.67	muscle	data sparse or not reliable
Freshwater fish	16	W (0.05-4.0?)	W 20.0	muscle	data sparse or not reliable
Mollusca	16	----	----	----	data sparse or not reliable
Crustacea	5	----	----	----	data sparse or not reliable
Echinoderms	4	----	----	----	data sparse or not reliable
Lower animals	10	----	----	----	data sparse or not reliable
Higher plants	67	D (<0.1-2.0?)	D 2,165.0	leaf	good bio-indicator
Lichens	6	----	----	----	data sparse or not reliable
Fungi	1	----	----	----	data sparse or not reliable
Algae	12	D (0.0-1.5)	D 6.0	whole	data sparse or not reliable
Total	157				

D = dry weight, W = wet weight, in ppm

methods. It is of interest that two species of oysters were found to have high levels of Sn^{113} in nuclear reactor waste in India (Patel and Ganguly 1973).

Higher Plants

Tin has been determined in 67 species of higher plants in a recent period, so that valid data are available for review. Higher plants found in areas with high tin concentration such as in Malaya frequently have high levels of Sn. Most of the high levels are found in plants near Sn smelters, tailings areas and slime holding ponds, slag heaps or sludge-amended soils.

Certain plants accumulate fairly high levels and those around tin smelters may have very high levels, up to 2,165.0 ppm dry weight in *Ehretia microphylla* in Malaya (Peterson et al. 1979). While the plants were washed before analysis, it was not determined whether some of the Sn was external contamination. Of 123 collections of spanish moss, six contained Sn of which four were in the areas of the only tin smelter in the United States.

Twelve species of plants have been used to measure environmental gradients of Sn. These species (except one) were used to measure gradients from a tin smelter, mining and placer operations. Also, a variety of species have been used in various countries as indicators of economic deposits of tin. Certain mangrove species have been well studied for this use. There are insufficient data to determine background levels of tin in vegetation. Some measurements by Schroeder et al. (1964b) in Vermont indicate fairly high levels for some plants e.g. asparagus 9.07 ppm wet weight, and for oats, beans, peas and alfalfa. Whether these resulted from pollution by fertilizer and other sources is unknown. Many canned foods have been analyzed and very high levels of Sn have sometimes been found, particularly those that are highly acid or have high nitrate contents (some of these have caused tin poisoning).

In summary, there are certain species of plants and animals with potential for biological monitoring organisms of tin. These include certain predatory freshwater fish as northern pike, and certain species of higher plants such as species of mangrove and spanish moss. More studies are needed with accurate recent measurements before a comprehensive assessment can be made of potential monitoring organisms.

Vanadium

A total of 302 species of plants and animals have been analyzed for concentrations of vanadium. Of these, 161 species are animals and 141 species are plants (Table 40). Many of the studies especially for tunicates were made before accurate analytical measuring equipment was available. These data are included in the compilation but should be used with caution. There is a tendency for recent more accurate data to be lower than early determinations. For most groups the useable data are too sparse and variable to allow good selection of potential monitoring organisms.

TABLE 40. SUMMARY OF VANADIUM LEVELS IN PLANTS AND ANIMALS

	No. Species	Baseline Non- or Little Contam.	Contam. Area (maximum)	Tissue	Remarks
Mammals	19	W (0.0-1.2)	W 6.82	fat, kidney	
Birds	5	----	W 13.85	fat	data sparse
Marine fish	21	W (0.0-1.0?)	D 9.0	muscle and bone	data sparse
Freshwater fish	14	W (0.05-2.4?)	W 3.4	muscle and bone	
Molluscs	21	----	D 130.0?	shell	data sparse and suspect
Crustacea	12	----	A 45.0?	whole	data sparse and suspect
Tunicates	45	highly variable	A 185,000	blood	early data
Lower animals	25	highly variable	A 1,230.0	blood	early data
Higher plants	100	D (0.0-10.0)	A 4,000.0	root, leaf, etc.	
Moss, lichens and fungi	9	----	A 2,000.0	----	data sparse
Algae	32	D (0.3-3.0)	D 21.3		
Total	302				

D = dry weight, W = wet weight, in ppm

Mammals and Birds

Since vanadium is not readily absorbed nor deposited in mammals they are probably not good biological monitors. There is no good evidence of predatory animals having higher levels of vanadium. The kidney and fat tissue, and perhaps teeth may be the best tissues for analyzing concentrations of V. The guinea pig was apparently effective in measuring an environmental gradient of vanadium. No specific mammals or birds are presently recommended for monitoring vanadium.

Marine and Freshwater Fish

The levels of vanadium in fish are somewhat variable. There is limited evidence for calico bass that there is any accumulation correlated with higher environmental levels of vanadium. The available data do not allow selection of any species for potential use for biological monitoring. More data should be obtained for northern pike, trout, walleye, and calico bass. Muscle and bone tissue appear to have the highest levels of vanadium.

Mollusca

The available data for 21 species of molluscs indicate that some species accumulate vanadium. Deep sea scallops were used to monitor ocean dump sites of acid wastes from a titanium oxide plant and a sewage sludge dump site off the mid-Atlantic coast of the United States. The levels of V in scallops in and south of the dump site were compared with levels of scallops north (upstream of the Gulf Stream) and were significantly higher in and below the site (Pesch et al. 1977).

Levels of vanadium were high in oyster, mussel and scallop tissues measured by Brooks and Rumsby (1965) using spectrographic analysis. Levels of vanadium for shells were very high. Deep sea scallops appear to have promise for biological monitoring and probably mussels and oysters, but more confirmatory data are needed.

Crustacea

Most of the data on crustacea are based on earlier determinations so that there is not sufficient information to select any species for potential biological monitors.

Tunicates

Tunicates and ascidians are marine sea squirts and related organisms which were shown in 1911 to accumulate and concentrate vanadium in high concentrations especially in the blood. Since then, 45 species of tunicates have been measured for V content. Values up to 185,000 ppm ash weight have been determined in tunicate blood. Goldberg (1951) using V^{48} showed that the tunicates could obtain all of the vanadium from seawater to concentrate the element to observed levels. While the data on vanadium in tunicates is extensive, it was mostly done earlier this century, with the latest in 1963, so that some confirmatory work with recent more accurate methods of analysis appears advisable. However, certain groups of families show high concentrations and could perhaps be used for monitoring if they are proven to correlate with environmental levels. Presently, it appears that tunicates concentrate high levels without regard to pollution or environmental gradients, so that none are recommended for biological monitoring.

Echinoderms and Lower Animals

Some sea cucumbers accumulate high levels of vanadium but have not been shown to correlate with high environmental concentrations. Certain other lower animals such as bryozoa have the same capability, but none are presently recommended as potential biological monitoring organisms.

Higher Plants

Of the 100 species of higher plants which have been studied for vanadium content, many show high levels correlated with high environmental levels, especially in uranium ore country where vanadium is found more highly concentrated (Cannon 1960, 1963, 1964, 1969). Various species of plants show fairly high concentrations of V including bunch grass and big sage used for measuring the environmental gradient of vanadium from a phosphate processing plant in Utah. Spanish moss proved to be an excellent monitoring plant for measuring environmental gradients of V from industry and commerce. Some of the most promising higher plants to consider for potential biological monitoring organisms could include bunch grass, sagebrush, locoweed, saltbush, juniper, parsley, paintbrush, rabbit brush, indian rice grass, oak and spanish moss. Leaf and root tissue appear to have the highest concentrations of vanadium. No studies are known to have measured the external contamination of plants resulting from air deposition. However, nearly all of the vanadium in spanish moss would result from air deposition (to 500.0 ppm ash weight).

Mosses, Lichens and Fungi

Mosses, lichens and fungi all show high concentrations of vanadium in the nine species studied. The fungus *Amanita muscaria* with up to 181.0 ppm dry weight has a very high level. It has been shown in two species of lichens and several species of mosses that the high levels of these plants are correlated with increased gradients of vanadium in the environment, including increase over a period of 24 years. Several species of liches and mosses can be recommended for potential biological monitoring of vanadium including use of transplants and moss bags.

Algae

Many of the 32 species of marine algae which have been measured have high levels of vanadium. None of the species are known to be useable for correlating with environmental gradients but this needs to be studied. Some of the high levels of vanadium in algae in Tokyo Bay and the Sea of Japan may result from contamination, but this was not shown in fairly extensive studies by Saenko et al. (1976) or Gryzhankova et al. (1973). No algae are presently recommended for biological monitoring of vanadium but several species could have promise.

SUMMARY

The data on bioaccumulations and bioconcentrations of trace metals compiled in Volume 2 have been analyzed with regard to potential biological monitoring organisms. Data on use of organisms for monitoring environmental gradients of trace metals, relationships in food chains, and biotransformation of trace metals were also considered. A very large number of potential biological monitoring organisms were found which are briefly summarized in

Table 41. The organisms or taxonomic group of organisms with selected organs and tissues are presented with a broad rating system indicating the relative values for biological monitoring. Data for human hair are taken from the review under this contract by Jenkins (1979).

TABLE 41. POTENTIAL OF SELECTED ORGANISMS FOR BIOLOGICAL MONITORING

	Human and Animal Hair*	Mammal Organs	Bird Feathers	Bird Organs	Fish	*Mytilus edulis* or Other	Higher Plants	Moss and Lichens	Algae
Antimony	E	liver, G	—	—	P	P Arbacia, G	Rose, E	—	—
Arsenic	E	kidney, G	G	liver, P	G	E	E	—	E
Beryllium	—	P	P	P	—	G	G	—	—
Boron	—	bone, P	—	—	—	G, coral crustacea	E	—	—
Cadmium	E	kidney, G	P	kidney, liver, E	G	E	E	E	E
Chromium	E	spleen, E	—	—	P	G	E	E	G
Cobalt	—	—	—	—	P	E	E	—	G
Copper	G	liver, G	G	liver, G	P	oyster, E	E	E	E
Lead	E	kidney, bone, E	E	femur, E	P	E	E	E	E
Mercury	E	liver, E	E	liver, E kidney, liver, G	E	E	G	G	P
Nickel	G	liver, P	—	kidney, G	G	G	E	E	G
Selenium	G	kidney, G	G	liver, G	P	—	E	—	—
Tin	G	kidney, P	—	kidney, G	fresh-water, G	—	E	—	G
Vanadium	G	liver, G	—	—	P	tunicates, E	E	E	G

* from Jenkins (1979)
P = Poor
G = Good
E = Excellent
— Insufficient data

SECTION IV

BIOLOGICAL MONITORING ORGANISMS

Analysis of the compiled data on accumulation of trace elements in plants and animals (Volume 2) together with review of use of organisms for monitoring environmental gradients of trace metals, and their role in food chains has resulted in a rather extensive list of potential biological monitoring organisms (summarized in Table 41). Review of these organisms requires consideration of the needs, requirements, and priorities previously established (Table 4) and of the eight selection criteria. In addition, final selection also requires consideration of the monitoring objectives, which are exposure assessment monitoring, environmental and food surveillance, and minimum global baseline surveillance.

Exposure assessment monitoring includes monitoring man, the immediate environment of man, and selective environmental monitoring directly related to critical sources and pathways. The major requirements are for biological monitoring of lead and cadmium, and also of arsenic, mercury, and nickel as required. Special conditions may require biological monitoring of any toxic trace element or combination of elements.

Surveillance monitoring of certain toxic trace metals is required to a) establish baselines, b) estimate trends, c) evaluate effectiveness of management and regulatory decisions, and d) support an early warning system for trace metal hazards and problems. Surveillance monitoring can be conducted on a global, national or regional, or local area scale on various organisms in the environment including food organisms. The priorities recommended for surveillance monitoring are as follows:

	High Priority	Limited Priority
Global	Pb	Cd and As
Regional or National	Pb,Cd,Hg,As	Ni,Se,V
Local	Pb,Cd,As,Hg,Ni	Sb,Be,Cr,Co,Cu Se,Sn,V
Food	Cd,Pb,Hg,As	Co,Cu,Ni,Se and Sn

These biological monitoring needs and priorities require selection of a limited number of biological monitoring organisms and tissues that best fulfill these requirements and objectives, and best fit the eight selection criteria. While there are many organisms which can be used, the potential monitoring organisms which presently appear to fit these requirements best are:

- For monitoring man himself
A. Human hair

- For monitoring the immediate environment of man
B. Rats
C. Pigeons
D. Domestic animals
E. Higher plants, food plants and crops

- For monitoring the terrestrial environment
  - Atmosphere
F. Mosses and lichens
  - Soil and air
E. Higher plants
  - General
G. Birds
D. Domestic animals

- For monitoring the aquatic environment
  - Marine
H. Marine algae
I. Molluscs -- *Mytilus* and oysters
J. Fish (for food surveillance)
  - Freshwater
I. Molluscs (?)
J. Fish (for food surveillance)

The eight selection criteria were reviewed for each of the selected monitoring organisms. These include the various metals accumulated, common, widespread geographically, easily collected, adequate size and resampling tissue, occur in impact and unpolluted areas, correlation with environmental levels of trace metal, and available background data. The trace metals accumulated, and the degree of fulfillment of the selection criteria are summarized in Table 42. The remarks in this table show any lack of fit with the criteria or any problems encountered. The summary shows that more data are needed on background and effects of environmental factors, and more studies are required on monitoring environmental gradients for some metals for the rat, pigeon, and other birds and freshwater molluscs. Fish are relatively poor biological monitoring organisms, except perhaps for mercury, but are suitable and needed for food surveillance monitoring.

Use of two or more of the organisms or tissues jointly or concurrently would be highly advisable to check on the other organism(s) or tissues. In the marine environment it would be desirable to monitor the soluble trace metals (by marine algae) and the particulate and sediment component (by molluscs).

The selected monitoring organisms are reviewed with regard to their potential use, advantages and disadvantages. All of these organisms are not

TABLE 42. SELECTED BIOLOGICAL MONITORING ORGANISMS IN RELATION TO SELECTION CRITERIA

Monitoring Organism (tissue)		Trace Metals Accumulated*	Remarks on Selection Criteria
Human hair		Sb, As, Cd, Cr, Pb, Hg (Cu, Ni, Se, Sn, V)	fit all criteria
Rat	hair	same as human	need more background data and gradient studies for some metals
	organs	Cr, Pb, Hg, Cd, As	
Domestic animals		same as rat	fit all criteria
Pigeon	feathers	Pb, Hg (As, Cu, Se)	need more background data and gradient studies for some metals
	organs	Cd, Pb, Hg (Cu, Hg, Ni, Se and Sn)	
Starling, sparrow		same as pigeon	mainly temperate area, need more background data
Fish, freshwater		Hg (As, Ni, Sn)	need more background data and gradient studies
Fish, marine		(As, Cd, Hg)	need more background data and gradient studies
Molluscs		As, Cd, Co, Pb, Hg (Be, B, Cr, Cu, Ni)	marine fit all criteria; freshwater need more background data and gradient studies
Higher plants, food crops		all but (Be and Hg)	fit all criteria
Mosses and lichens		Cd, Cr, Cu, Pb, Ni, V (Hg)	may be absent in impact areas, can be transplanted
Marine algae		As, Cd, Cu, Pb (Cr, Co, Ni, Sn, V)	fit all criteria

*Trace elements listed show excellent accumulation except those in parentheses (good or fair) recommended for use for monitoring, but are selected as those organisms that appear to have the best potential.

Global baseline surveillance of trace metals using a few carefully selected organisms is needed to establish world baselines and trends, and to discover any "hot spots" or unknown hazards. The highest priority trace metals for global monitoring would be Pb, Cd, Hg and As, but all other trace metals should be considered.

HUMAN HAIR

To accurately assess human exposure, measuring levels of toxic trace metals in man himself is the best biological monitoring possible. This requires measurement of a part or product of man without damage, and minimum inconvenience. The potential monitoring tissues or products are: hair, nails, ear wax, saliva, urine, feces, sweat, semen, blood, teeth, milk and placentae. All of these with perhaps the exceptions of ear wax and semen have been considered for monitoring (EPA 1976). The various tissues and products all have particular advantages and disadvantages for use.

Analysis of the trace metals in feces measures that exposure component which is not absorbed and is excreted. The milk, urine, saliva and sweat measure the component that is absorbed but excreted. The blood measures the component absorbed and temporarily in circulation before excretion and/or storage. The component in placentae and semen is not easy to categorize, but trace metals in placentae have been studied.

The hair, nails and teeth are tissues in which trace metals are sequestered and/or stored. Trace metals have been measured in teeth, but these are not available for regular monitoring and only certain metals are stored, so that their value is limited. Hair and nails have been quite fully evaluated for use in biological monitoring and the results of their uses, values and limitations have been recently reviewed by Jenkins (1979). While problems exist, the consensus of specialists is: "if human hair samples are collected properly, cleaned and prepared for analysis correctly, and analyzed by the best analytical methods using standards and blanks as required, in a clean and reliable laboratory by experienced personnel, the data are reliable." Most of these requirements are equally true for analysis of trace metals in most biological specimens. A problem of importance is the possible external contamination of hair by trace metals from soap, shampoo, dyes and other chemicals, and from external pollution. Methods have been developed to wash or treat the hair for removal or evaluation of this contamination.

It was concluded on the basis of a rather comprehensive compilation and analysis of data including use of hair for measuring environmental gradients of trace metals that hair has good potential for biological monitoring. Of the 14 trace elements considered in this report, human hair is excellent for biological monitoring of arsenic, cadmium, chromium, lead and mercury, and quite good for monitoring antimony, copper, nickel, vanadium and perhaps selenium and tin. However, for boron and cobalt, human hair is either not meaningful or has not been studied sufficiently. The details of sample collection, cleaning and sample analysis, the advantages and disadvantages of using hair, and the effects of the factors of: a) location and type of hair on the body, b) age, c) sex, d) hair color and e) concentration variation in hair in relation to distance from the scalp, are reviewed in Jenkins (1979).

Human hair has been selected as one of the important monitoring materials for worldwide biological monitoring in the Global Environmental Monitoring System (GEMS) of the United Nations Environmental Program. Also an international program using human hair for monitoring trace metals has been initiated by the International Atomic Energy Agency (IAEA 1977).

Human hair is a tissue which is easily obtained, easily stored and transported. It shows the exposure to trace elements for several months to about a year, and the level of some metals in the body. It is also very good material for storing in tissue banks (Jenkins 1977). Samples of hair over 100 years of age have been analyzed. Hair is highly recommended for biological monitoring of man, especially in combination with analysis of other human organs, tissues or products.

Human nails have been used in a program of the World Health Organization for monitoring trace elements in humans (IAEA/WHO 1975). The uses of human fingernails and toe nails for monitoring and the data on levels of trace metals in nails have been reviewed by Jenkins (1979). Human nails are suitable for biological monitoring, but there is much less experience and more problems with using nails in comparison with human hair.

In summary, human hair can be used effectively for biological monitoring of the highest priority toxic trace metals — lead, cadmium, mercury, and arsenic. Hair can be used to monitor the other trace metals of local significance, nickel, antimony, chromium, copper and vanadium and perhaps selenium. Not enough is presently known about beryllium, boron and cobalt in hair for use in monitoring. Human hair fits all of the selection criteria: a) all important trace metals are accumulated, b) it is common, c) it is widespread geographically, d) it is easily collected and handled, e) it is of suitable size and can be resampled, f) it occurs in impact and unpolluted areas, g) there is correlation with environmental gradients of the metals, and h) there is sufficient background and experience data. Hair is especially suitable for biological monitoring for exposure assessment as well as global, regional, and local surveillance monitoring.

RATS

Rats are abundant pests closely associated with man throughout the world. The major pest species are the Common rat *Rattus rattus*, the Norway or Brown rat *Rattus norvegicus* and the Roof rat *Rattus alexandrinus*. Rats are abundant in cities, especially in older ghetto areas. They feed on about the same food as humans, are closely associated with humans and probably receive about the same environmental exposure to trace metals. Some rats may be exposed to more lead in street dust. Rats are found wherever there is adequate food, especially near stored food supplies, garbage cans and garbage dumps. They live in the same houses with man and therefore are probably the best biological organisms for monitoring the immediate vicinity of man, except perhaps the cockroach.

Much is known about toxic trace metals in rats, and data are available on concentrations and accumulation of As, Be, Cd, Cr, Co, Hg, Pb, Ni, Se and V. In addition, much is known about the intake, accumulation, excretion, retention time, effect of age and sex and other factors in the laboratory rat. Of special value are the extensive data on exposure and toxicity assessment which permits fairly accurate extrapolation of effects of toxic metals in relation to man. Rats have a tenfold higher oxygen consumption to body weight ratio compared with man (Mouw et al. 1975), which amplifies respiratory exposure.

Rats have been used effectively by Mouw et al. (1975) for measuring environmental gradients of lead. Urban Norway rats in Detroit had 20 times the lead in bone and kidney tissue as rural rats. It was stated that since older rats did not exhibit increased lead accumulation they were probably in a steady state regarding lead input and output. Rat bone in Detroit had 200.0 ppm wet weight and bone in rural rats had 10.3 ppm wet weight. Mouw et al. (1975) state:

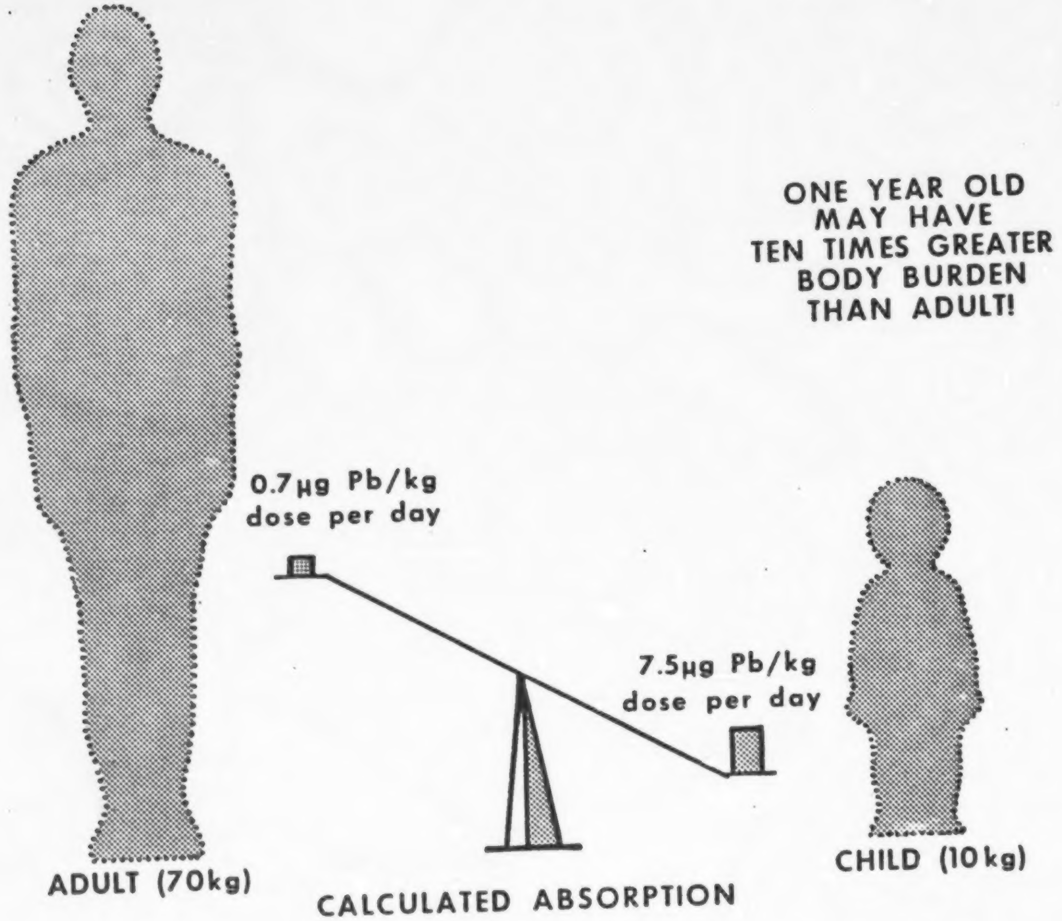
> "The most striking finding of this study is the extremely high accumulation of lead in the urban rats; the tissue levels of lead in the rural animals are much lower and similar to tissue levels reported for adult humans. This confirms our hypothesis that rats (compared with humans) would serve as a more sensitive index of environmental lead. . . . Children might represent an intermediate degree of exposure to airborne lead between adult humans (breathing air 1.5 meter above the ground) and urban rats (breathing air at ground level). Thus the urban rat could be a useful model for sensitive monitoring of the potential accumulation of airborne lead to man."

A comparison of lead absorbed by children and by adults makes this model even more useful (EPA 1976), "Taking into account body weight, the resulting body burden of lead calculated for the child (Figure 1) is about 10 times more per kilogram of body weight than for adults. This calculation does not include the additional exposure to lead children are subjected to from such sources as street and house dust which may be critical sources in some populations of children."

The urgency and priority of studying and monitoring the lead problem of the critical target population -- city and ghetto children -- is considered to greatly outweigh all other monitoring needs and requirements.

Rats have also been used for monitoring the presence of mercury. The Norway rat was found to contain 95.0 ppm wet weight of mercury in the liver, when exposed to contamination at a farm granary in Sweden (Lihnell and Stenmark 1967). Laboratory rats have been used in studies on cadmium which resulted in life-shortening and osteoporosis (Schroeder 1974).

Rat hair or fur could be used effectively for monitoring certain trace metals. Mammal hair (other than man) has been used effectively for monitoring



CALCULATED ABSORPTION

Daily Intake	Lead Absorbed
Food - 300 µg	30 µg (10%)
Water - 20 µg	2 µg (10%)
Air - 2.5 µg (23 m^3)	21 µg (37%)
TOTAL	±53 µgPb

$$\frac{53\ \mu gPb}{70\ kg\ man} = 0.7\ \mu gPb/kg \text{ dose per day to man}$$

Daily Intake	Lead Absorbed
Food - 130 µg	65 µg (50%)
Water- 10 µg	5 µg (50%)
Air - 2.5 µg (6 m^3)	5.5 µg (37%)
TOTAL	±75.5 µgPb

$$\frac{75\ \mu gPb}{10\ kg\ child} = 7.5\ \mu gPb/kg \text{ dose per day to child}$$

Figure 1. Calculated lead body burden comparison between adult and child.

environmental gradients of As, Cd, Cr, Pb, Hg but not for Cu (Jenkins 1979). Rat hair can probably be used to monitor the same elements as listed for human hair. Possible external contamination, especially lead, would have to be assessed and removed, using techniques presently available. Monitoring of trace metals in additional organs especially the kidney, liver and bone should also be considered.

Rats fit the selection criteria quite well. They appear to be excellent biological organisms for monitoring the highest priority toxic trace metals, especially lead. Collecting and sampling rats is highly successful for personnel with the specialized skills. Rats can be trapped or poisoned (with non-metallic poisons). They occur in circumscribed home ranges and with the exception of shipboard rats are not migratory.

It is strongly recommended that a pilot research monitoring program be established with high priority to determine the value and effectiveness of rats for biological monitoring. They have very good potential for use for direct exposure assessment monitoring of man, and especially exposure of children to lead.

PIGEONS

The Domestic pigeon or Rock dove Columba livia is a widespread non-migratory ubiquitous species usually closely associated with man in both urban and rural sites. It occurs in many of the cities of the world often in bothersome numbers. It is primarily herbivorous and feeds on grains, leftover food, and other organic material. Pigeons are usually relatively sedentary with limited mobility. They inhabit the most densely populated areas with heavy vehicular traffic. They are exposed to similar levels of air pollution and perhaps more dust than man. Pigeons have been studied in metropolitan areas in relation to lead pollution by Tansey and Roth (1970), Siegfried et al. (1972), and Ohi et al. (1974). Tansy and Roth found higher levels of lead in various organs especially hard tissue of pigeons in Philadelphia than in rural pigeons. Ohi et al. (1974) found higher levels of lead in the femur, kidney and blood, and lower ALA-D activity in pigeons in crowded areas and in a bus terminal in Central Tokyo than in suburban Tokyo or rural areas.

Pigeons have been shown to be effective in accumulating mercury. In Columba sp. in Ireland, Eades (1966) found (0.015 to 5.33) ppm. In the Stock dove Columba oenas in Norway, Holt (1969) found 0.6 ppm wet weight in muscle. In the Wood pigeon Columba palumbus he found (0.78 to 4.8) ppm in the kidney with 7.1 percent over 2.0 ppm. In pigeons in Sweden, Borg (1970) found (0.1 to 40.0) average 2 ppm wet weight in the liver. In Finland, Karppanen et al. (1970) found (0.1 to 0.3) average 0.2 ppm in muscle tissue. In Sweden, Lundholm (1967) reported (0.5 to 2) ppm in the eggs. In Columba livia in Mississippi, Knight and Harvey (1974) found (0.006 to 0.23) median 0.22 ppm wet weight of Hg in the brain, (0.022 to 0.07) median 0.049 ppm in the feathers, (<0.005 to 0.009) ppm in the liver (<0.005 to 0.051) median 0.02 ppm in muscle, and (0.029 to 0.059) ppm in the claws during the first week of captivity. In Norway, Holt (1969) in the same species found (1.0 to 2.1) ppm wet weight of Hg in the kidney.

Bird feathers are excellent tissues for studying mercury and lead levels. They are good for measuring levels of arsenic, copper and selenium, but poor for cadmium and beryllium based on incomplete present knowledge. They are also excellent for measuring manganese and zinc according to Kelsall (1970). The liver is excellent for measuring cadmium and good for lead, nickel, selenium and tin. Eggs and egg shells can be used for monitoring.

After the ban on use of alkyl mercury for seed coating in Sweden, Wanntorp et al. (1967) showed that there was a marked decrease in mercury in the liver of the Wood pigeon Columba palumbus. There was also a marked decrease in mercury in feathers of about eight other species of birds in Sweden following this ban (Westermark et al. 1975). Measurement of mercury in feathers of various species of birds from specimens from 1830 to the present showed an increase of mercury correlated with use of seed dressing of alkylmercury (Westermark 1967). It was estimated that mercury in feathers was seven to eight times greater than in muscles.

For global biological monitoring of lead, pigeons are better than starlings because of their wider geographic distribution, more sedentary habits and closer association with man. Use of feather analysis would permit sampling the same trapped birds without killing them.

Pigeons fit the selection criteria quite well. There have been a number of studies that show that pigeons are effective in monitoring environmental gradients of lead and alkyl mercury. They are easily collected and handled and deserve consideration for both exposure assessment and surveillance monitoring. While they probably are not as good as rats for biological monitoring, it is recommended that a pilot research monitoring program be established to determine their effectiveness and use. Pigeons could be good complementary organisms to use with rats for monitoring.

DOMESTIC ANIMALS

The domestic animals which could be considered for biological monitoring organisms include the most common widespread species on which there is an abundance of information and data. The domestic animals selected include two species used for food, the cow and the pig. Other domestic animals selected for biological monitoring are the cat, dog and horse. These animals are closely associated with man in rural areas, and in addition, the cat and dog occur in urban areas. Each of these animals has certain valuable attributes for biological monitoring, but are probably not as good as the rat.

1. The cow, Bos bovis, has been extensively studied with regard to trace metal accumulation, especially in milk and hair which can be obtained for resampling of the same animal. Also quantities of organs such as the liver and kidney can be obtained from slaughter. Cows are regularly sampled by the U.S. Department of Agriculture (USDA) in the food and feed pesticide surveillance monitoring program jointly with the Food and Drug Administration (FDA) for As, Cd and Hg. Trace metal accumulation of As, Be, Cd, Co, Cr, Cu, Pb, Hg, Ni, Se and V have been studied in the cow. The cow is here being suggested for additional exposure assessment biological monitoring using hair

and other tissues and milk as used by Dorn et al. (1973), Lewis (1972), Munshower (1972) and Anke et al. (1976), for monitoring environmental gradients of cadmium. Additional studies by Dorn et al. (1974), Orheim et al. (1974), Lewis (1972), Mollenhauer (1972), and others for lead are examples of rather extensive use for exposure assessment monitoring. The cow appears to be a good biological monitoring organism for both surveillance and exposure assessment monitoring and fits the selection criteria quite well.

2. The pig, Sus scrofa, is an abundant omnivorous domestic animal that is raised throughout the world for food and other products. It has been fairly well studied with regard to trace metal accumulation, and levels of As, Cd, Co, Cr, Cu, Pb, Hg, Ni, Se, Sn and V have been determined in various tissues. Pigs were studied in a New Mexico case of mercury poisoning of a human family due to eating pork from pigs fed mercury-treated grain (Curley et al. 1971). Very high levels of Hg were found in the pig brain, liver, kidney and muscle. There would probably be a large difference in the levels of trace elements in pigs depending on whether they were raised on a farm and fed primarily on grain, or fed on various plants and animals when free ranging on farms, or whether fed on garbage and swill. Pigs have not been studied as extensively as cows or horses with regard to trace metals and cannot be recommended as highly. However, various tissues from pigs are presently being monitored in the United States food surveillance program.

3. The horse Equus caballus is abundant throughout the world and is closely associated with man in rural and suburban areas. Horses have been rather well studied with regard to accumulation of toxic trace metals and levels of As, Cd, Co, Hg, Ni and V have been determined. A major reason for interest in horses for biological monitoring is that they accumulate large quantities of certain toxic metals, especially fallout around smelters. Horses have died as a result of eating grass and hay that was heavily contaminated by lead or cadmium in the vicinity of smelters in Wales (Goodman and Roberts 1971), California (Knight and Burau 1973), and other areas. The mane has been used by Lewis (1972) to successfully measure environmental gradients of As, Pb and Cd from a Pb smelter, and by Goodman and Roberts (1971) for Pb from a smelter.

Horses are not being measured in any surveillance monitoring in the United States since they are not recognized as an important food item. Horses accumulate various trace metals in the mane, hair, liver, kidney and bone. The mane could be used for resampling. The horse fits all the selection criteria and could be effectively used for either surveillance or exposure assessment monitoring.

4. The cat Felis domesticus is an abundant pet animal that occurs worldwide and is closely associated with man. It may eat the same food as man, or special cat food, and additional items such as mice and other small animals around human habitation. Since the cat frequently licks its fur, it could also accumulate additional levels of external contaminant trace elements such as lead.

Detailed studies have been made on mercury in cats, especially in the Minamata disease outbreak in Japan (Takeuchi et al. 1962), and in Ontario, where cats ate fish contaminated by mercury from a chlor-alkali plant

(Takeuchi et al. 1977). In both areas, the cats had very high levels of Hg in the hair, kidney and liver. Lead levels have been studied in blood of cats in New Zealand by Ward et al. (1977). There is not an adequate background of data on trace metal accumulation in cats and much more research would be needed before they could be used for biological monitoring. Sampling of hair would be the best method because it permits resampling of the same individuals. Cats appear to fit the selection criteria quite well for use for exposure assessment monitoring. However, much research is needed and the problem of the effects of the type of diet would have to be considered.

5. The dog *Canis familiaris* is one of the most abundant domestic animals in the world. It is found anywhere that man lives and is closely associated, eating the same food, or special dog food, sometimes supplemented by a diet of small animals, garbage and carrion. The diet of the dog would usually give a fairly wide sampling of human food. Dogs lick their fur and could ingest external contaminant trace metals. Trace metal accumulation has been fairly well studied in dogs including Cd, Co, Hg, Pb, Se and V. A number of cases of lead poisoning of dogs have been described by Zook et al. (1972), Wilson and Lewis (1963), and Ward et al. (1977). Cd was determined in the liver and kidney of dogs in Vermont (Schroeder et al. 1967). Mercury was found to be high in dogs in the arctic that fed on fish and seal (Smith and Armstrong 1975). Co and Se were measured in blood by Lindberg and Lannek (1970) and vanadium was found to be high in dog teeth in Germany (29.0 to 41.5 ppm ash weight) by Durr (1969).

Dogs fit the selection criteria quite well but more background data are needed for most of the elements. More research on use for monitoring environmental gradients of trace elements is also required before dogs should be used for biological monitoring.

In summary, cows and pigs are presently being monitored in the United States in the food surveillance monitoring program. Cows and horses appear to have promise for exposure assessment monitoring of man. Use of pigs, cats and dogs for biological monitoring would require more background data including effectiveness of use for monitoring environmental gradients of trace metals.

HIGHER PLANTS, FOOD PLANTS AND CROPS

Higher plants or flowering plants are found throughout the entire world and many species, especially crop and ornamental species, are closely associated with man. There has been an enormous amount of research done on the accumulation of trace metals in higher plants and all of the selected metals are accumulated by various species. Cr, Cu, Pb, Ni and Se are often bioaccumulated to very high levels in certain species while As, B and Cd are accumulated to fairly high levels and Sb, Be, Co, Hg, Sn and V show only limited or selective accumulation.

An important problem is selection of specific species that accumulate the highest priority trace metals, and that are common and widespread over the world. Most species of higher plants have relatively limited distribution, except plants that have been dispersed by man such as crop plants and weeds.

Important grains crops and vegetables probably have widest distribution. Rice is common throughout tropical and subtropical areas and wheat and oats mostly in temperate areas. Corn is found in both areas particularly in the American hemisphere. Vegetables such as beans, lettuce, tomatoes and onions are worldwide. Many types of grains and vegetables are presently being monitored in the food surveillance Market Basket Survey by the USDA and FDA in the United States.

Plants obtain trace metals from uptake from roots, absorption through stomata, and some through the leaf surface from air and atmospheric fallout. There is often a component of unabsorbed contamination on lead, stem and bark surfaces, especially in heavily polluted impact areas.

Many species of plants have been used for biological measurement of environmental gradients of most of the trace metals. An outstanding plant is Spanish moss *Tillandsia usnoides* which was used to measure all of the selected trace metals. However, its distribution is limited to southeastern United States, and some tropical areas. Various grasses, especially *Agrostis* and *Festuca* have been used successfully to measure environmental gradients. These grasses are common in the north temperate area and in some tropical areas.

Most plants are seasonal in temperate areas except certain evergreen broadleaved trees and shrubs, and conifers such as pine and spruce. However, some dead remnants of grass and other plants may have higher levels in the winter.

There are many species of plants that accumulate very high levels of certain trace metals or show effects or aberrations which make them valuable as biogeochemical prospecting indicators for locating underground deposits of specific trace metals. Most of these indicators are local indigenous species that are rarely widespread and are only locally common. Examples are *Astragalus spp*. for Se, and *Silene cobaltica* and *Crotalaria cobaltica* for Co (Cannon 1971).

Higher plants offer a plethora of species that can be selected for biological monitoring of specific trace metals in specific impact areas. They could be used for exposure assessment monitoring in most types of impact areas. Tables 11 to 26 show over 100 species that have been used successfully for monitoring environmental gradients. Volume 2 shows over 1,000 species which have ability to accumulate trace metals, of which several hundred could be used for surveillance monitoring in different areas. Since there is much food surveillance monitoring of priority trace metals in many species of fruit, vegetables and grains in the United States, it does not appear to be necessary to recommend any additional species at present.

While many species of higher plants appear to be excellent biological monitoring organisms for both surveillance and exposure assessment monitoring, none are presently selected since mosses and lichens appear superior for monitoring of atmospheric pollution by many of the selected trace metals. However, since there are insufficient data for determining the effectiveness of mosses and lichens for monitoring As, Be, B, Co, Se and Sn, there are many species of higher plants that could be used for monitoring these trace elements (see Section III).

MOSSES AND LICHENS

Mosses and lichens have been used extensively for monitoring trace metals. Methods have been developed for effectively using mosses for monitoring environmental gradients of trace metals, both locally around sources and for regional monitoring, and for showing historic trends in levels of trace metals.

Mosses and lichens are excellent for monitoring cadmium, chromium, copper, lead, nickel and vanadium and they are fairly good for monitoring mercury. There are insufficient data for determining their effectiveness in monitoring antimony, arsenic, beryllium, boron, cobalt, selenium and tin. A problem with using species of lichens and mosses in highly polluted areas for biological monitoring is that they are sensitive to sulfur dioxide and are often eliminated in the vicinity of a smelter, city or other sources of pollution, forming "lichen deserts" and "moss deserts."

Mosses and lichens lack roots and receive most of their nutrients and trace metals from atmospheric fallout from rainfall or by the impaction and sedimentation of airborne dusts. Absence or reduced cuticle permits ions retained on the surface to have direct access to exchange sites in the cell wall. Mosses function as natural ion exchange resins, with high cation exchange capacities due to the high polyuronic acid content of the cell walls (Knight et al. 1961).

Epipedic mosses growing on rock or soil substrates show some correlation with the trace element level of the substrate especially with high levels of the trace element; at lower levels there is little enrichment. When moss carpets grew on a developing or mature layer, no enrichment of heavy metals took place (Ruhling and Tyler 1970). Epiphytic mosses growing on tree bark did not correlate with trace elements in the bark of ash or beech trees (Rasmussen 1977).

Hypnum mosses were sampled along transect lines upwind and downwind from a smelter and urban-industrial area by Goodman and Roberts (1971). There was excellent inverse correlation of the trace metal levels of Pb, Cd, Cu and Ni with increasing distance from the source. They also pioneered an elegant technique of suspending moss in nylon mesh bags, using the mosses as indicators and integrators of atmospheric trace metal levels. Goodman and Roberts (1971) in evaluating their technique as useful indicators of airborne pollution stated, "Our methods are much more rapid, inexpensive, and probably more meaningful than spot-sampling of air by filtration for which prohibitive resources are needed for a few months operation." They also pointed out that more knowledge is needed on a) the relative bonding energies of the various metals on the exchange surface of Hypnum, b) the modifying influence of rainfall pH, and c) the relative contribution to uptake made by dry deposition (sedimentation and diffusion of various particle sizes) and wash-out processes via rainfall.

A simple inexpensive technique was developed for detailed monitoring of airborne lead, cadmium and zinc around a Zn Pb smelting complex using Sphagnum moss suspended in fine nylon hair nets from natural vegetation (Little and Martin 1974). Computerized maps were drawn of the levels and patterns of distribution of the metals collected by the moss bags. The authors' conclusions were: "Despite any theoretical problems involved in the validity of converting deposition rates from μg/g moss/day to tones/square km/month, moss bags have proved an invaluable, rapid, inexpensive and convenient practical means of diagnosing pollution and monitoring the patterns and intensity of heavy metal pollution using biological materials. Furthermore moss bags represent a means of monitoring which is, in many ways, more meaningful than deposit gauges or high volume air samplers in terms of contamination of crops and natural vegetation, especially as they may easily be suspended amongst the vegetation itself in large numbers."

The lichen Lecanora conizaeoides has been used to monitor environmental gradients of trace metals around a steelworks and an iron foundry. The order of the maximum trace metal enrichments for the lichen was Cd 74, Pb 62, Cu 35, V 31 and Ni 9 (dry weight) compared with levels in controls taken as regional background levels.

Transplanted lichens have been used by several authors to monitor trace metal pollution from the air. Pilegaard (1979) compared moss and lichen transplants (on pieces of branch or bark) exposed for seven months to atmospheric fallout and precipitation. The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the transplants were linearly correlated with fallout from the atmosphere, with mosses accumulating metals slightly faster than lichens. The metal concentrations in the transplants as well as bulk precipitation, followed a decreasing power curve when the distance to the steelworks was increased.

Mosses and lichens fit the selection criteria quite well except that they may not be present in highly polluted impact areas, but transplanting can be used effectively. Use of mosses and lichens is highly recommended for exposure assessment monitoring especially atmospheric pollution. They are also recommended for global, regional and local surveillance monitoring.

BIRDS

Various species of birds could be used for surveillance monitoring of national or local areas. Birds which are presently being monitored on a national basis in the United States are the Starling Sturnus vulgaris, using the body less feathers, skin, beak, feet and wings; the mallard Anas brachyrhynchos, and the Black duck Anas rubripes, using wings less feathers and distal joint. Monitoring results are discussed in Section V. The Woodcock Philophela minor was monitored in the eastern part of the United States only from 1970-1973, using liver and muscle tissue.

Species of birds, in addition to the pigeon, which could be used for monitoring could include crows, ravens, vultures and gulls which are omnivores and scavengers. While these birds accumulate high levels of trace metals, none of these can be recommended highly since all but ravens are migratory to some extent.

English Sparrow

The House or English sparrow Passer domesticus, an introduced species from Europe, is non-migratory and is found throughout the United States and much of Canada and Mexico. It is abundant on farms, in cities and in suburbs and is commonly found in the vicinity of man. It could serve as an alternate or additional species with the pigeon. The house sparrow feeds on grain, food scraps, animal feces and occasional insects.

House sparrows have been studied for lead content in Illinois by Getz et al. (1977a). The feathers contained 158.3 ppm dry weight in urban birds and 27.0 ppm dry weight of Pb in rural birds. Other tissues and organs also showed higher levels in urban birds. Chromium was found in house sparrows in Tennessee by Andren et al. (1973) and the whole body contained 1.0 dry weight. In Norway the house sparrow had 0.14 ppm wet weight of mercury in kidney tissue (Holt 1969).

House sparrows would have the highest priority for a biological monitoring species after pigeons. Much research is needed, but since these sparrows are not migratory the monitoring data would be comparable for different areas.

Starling

The starling Sturnus vulgaris is presently being monitored in the United States for mercury, lead, cadmium, arsenic and selenium. The starling is an introduced, abundant, widespread species found throughout the United States. Some populations of starlings are unfortunately migratory so that their value for biological monitoring is reduced. They are omnivorous, feeding mostly on crops, fruits and insects.

Starlings were used to compare the levels of lead in urban and rural areas in Illinois by Getz et al. (1977a). Feathers from birds in an urban area had 225.1 ppm dry weight and those from the rural area had 6.4 ppm dry weight. The femur in the urban area had 213.0 ppm dry weight and the rural area had 12.8 ppm. The kidney in the urban area had 98.5 ppm while the rural had 3.6 ppm dry weight. All of these comparisons were highly significant. Muscle tissue on the other hand had 2.4 ppm in urban and 0.8 dry weight in the rural area, which was not statistically significant at the 0.05 level. This is important in relation to the whole body analyses of the national starling monitoring program.

Starlings fit the selection criteria quite well except that some starlings are migratory.

Crow

The Common crow Corvus brachyrhynchos is an abundant pest species throughout the United States, except in arid regions, and occurs throughout the year. The common crow and related birds may have some potential for biological monitoring. They range over areas in feeding flocks. They are found throughout the United States but some populations of the common crow are migratory, which decreases their value for monitoring. The omnivorous crow is also a scavenger often seen feeding on animals killed on highways and roads. In Tennessee crows were analyzed by Andren et al. (1973). In the whole body there was 1.0 ppm dry weight chromium and 0.1 ppm dry weight of arsenic. The Hooded crow Corvus corone cornix in Norway had from 0.75 to 60.0 ppm with 12.9 percent over 2.0 ppm in the kidney (Holt 1969). In Sweden, Westermark (1967) found 35.0 ppm in the liver, 28.0 ppm in the kidney, 18.0 ppm in muscle, and 12.5 ppm in the brain. Ackefors (1971) also in Sweden, reported 29.0 to 110.0 ppm in the liver and kidney, and Lundholm (1967) reported 0.1 to over 20.0 ppm in the liver and 0.0 to 2.0 ppm in the eggs. No data on lead or cadmium were found for crows. Much more research and background data are required and pilot studies would have to be conducted to evaluate crows as candidates for use for biological monitoring.

The Common raven Corvus corax is frequent in the North and West of the United States especially near heavy timber. It is mostly a carrion feeding scavenger and is not migratory. Mercury was found in the raven in Ontario with 100 ppm wet weight in the liver (Fimreite 1974). The limited distribution decreases its value for monitoring.

MARINE ALGAE

Marine algae are among the most efficient and reliable biological monitoring organisms for monitoring estuaries and coastal marine areas, bays and harbors. They are excellent for measuring arsenic, cadmium, copper and lead. (Data for lead are somewhat variable.) They are fairly good for monitoring chromium, cobalt, nickel, tin and vanadium, but are relatively poor for monitoring mercury.

Marine algae have proven potential for biological monitoring under certain conditions. The algae are responsive only to the soluble trace metal components in the water and will not reflect the trace metals in food organisms and in organic or inorganic particulate matter. The biological half life of metals is high in algae and they can reflect the soluble concentrations of metals with a high degree of time integration (Phillips 1977). Cadmium and zinc are generally found mainly in the soluble fraction of water while lead, cobalt and iron are found mostly in particulate material.

Marine algae have been used to measure environmental gradients of arsenic, cadmium, copper and lead. They have also been found to correlate well with the levels of trace metals in some polluted areas, but more studies of this type are needed.

Sources of variation in trace metal concentrations in marine alga have been carefully studied. The main sources are a) variation with different species, b) increased concentration in older basal part compared with newer distal growth, c) seasonal variation (maximum usually in winter and spring) d) position of sampling on shoreline, e) salinity, f) water temperature, g) effects on growth of presence of metals, light, turbidity and nutrients, and h) competition between metals for binding sites. Data on these factors have been reviewed by Phillips (1977).

Marine algae fit the selection criteria quite well. They have real potential and demonstrated capability as monitoring organisms for exposure assessment as well as surveillance monitoring. Marine algae are complementary to *Mytilus edulis*, and oysters for biological monitoring of marine and estuarine habitats. The most promising marine algae for monitoring are *Ascophyllum nodosum*, *Enteromorpha spp.*, *Fucus spp.*, *Laminaria spp.*, *Ulva spp.* and perhaps *Sargassum spp.*

Marine algae could be used in a minimum global surveillance monitoring program with mussels and oysters in place of fish muscle planned by the Global Environmental Monitoring System (GEMS).

BIVALVE MOLLUSCS

Marine

Bivalve molluscs are very good and efficient organisms for biological monitoring of estuarine, coastal, bay and harbor and shallow seas. Various bivalve molluscs, especially *Mytilus edulis* and oysters are excellent for monitoring arsenic, cadmium, cobalt, copper, lead, mercury and vanadium. They are fairly good for beryllium, chromium and nickel.

Bivalve molluscs are filter feeders and obtain trace metals from a) food, b) from ingestion of inorganic and organic particulate material, and c) from solution. Planktonic food often has high trace metal content and is one of the main sources, however, elements in solution and particulate matter are also important. Lead, cobalt and iron are of especial importance in the particulates. Several studies have used radioactive elements to elucidate the source of trace elements in molluscs.

The sources of variation include age, weight and size. Older, larger molluscs may have higher concentrations but the rate of uptake of younger smaller specimens may be greater. Other factors are season, depth of sampling, salinity, temperature and coexistence of several trace metals. Data on effects of these factors have been reviewed by Phillips (1977), who also suggested that *Mytilus edulis* not be used for monitoring copper since it is handled atypically in comparison with oysters.

For monitoring open relatively shallow sea, scallops are good accumulators of certain trace metals although they are mobile. Bryan (1973) recommends their use for monitoring pollution in the sea.

For monitoring coastal waters, estuaries and harbors, oysters, clams and mussels are excellent accumulators. These are sedentary filter feeders which accumulate or concentrate the trace metal and do not appear to be seriously harmed by fairly large quantities. *Mytilus edulis* appears to be the mollusc of choice. Cockles, periwinkles and abalones are also good accumulators and may be considered. Carnivorous gastropods such as the dog whelk *Nucella* lapillus are fairly sedentary and acquire certain trace metals from food, which includes mussels and barnacles. The herbivorous limpets Patella spp. feed on rock encrusting lichens and marine algae in the intertidal zone, and have high levels of certain trace metals in polluted areas. Stenner and Nickless (1974b) transplanted limpets from an unpolluted site to a heavily polluted area in the Bristol Channel, and some trace metal levels increased greatly in three months.

Use of Mytilus edulis and oysters was proposed by Goldberg (1975) for monitoring pollutants including toxic heavy metals, in a program named "Mussel Watch." A workshop was held in Spain (Ellis 1979) to help implement this program which is discussed in more detail under global monitoring, Section V.

Mytilus edulis and various oysters fit the selection criteria quite well. They could be used for exposure assessment and environmental and food surveillance monitoring on a global, regional, or local scale. The use of Mytilus edulis and oysters for one of the few carefully selected organisms for global biological monitoring is an excellent choice, and would be better than use of fish muscle planned for the Global Environmental Monitoring System (GEMS).

Freshwater

Bivalve molluscs are commonly found in freshwater rivers and streams, lakes and ponds. There are many species, most of which have relatively limited distribution. Species in 18 genera of molluscs in freshwater have been analyzed for different trace metals. Those generea for which the most trace metals have been found include Amblema with Pb, Cd, Cr, Cu, Co and Ni, Anodonta with Pb, Hg, Cu, As, Ni and Cd, and Fusconaia with Pb, Cr, Cu, Co, Ni and Cd. Anodonta grandis was used successfully by Smith et al. (1975) to measure an environmental gradient of mercury from a chloralkali plant.

The trace metals found in the terrestrial pulmonate snail Helix include Cu, Cd, As, Pb, Sb and Sn. Helix aspersa was used successfully by Coughtrey and Martin (1976) to measure environmental gradients of Cu, Cd, and Pb from a smelter.

While there is an abundance of data on accumulation of trace metals in marine species of molluscs, there are relatively limited data for freshwater molluscs and much research is needed before they could be used effectively for monitoring freshwater. Sampling of freshwater molluscs was planned earlier in the National Pesticide Monitoring Plan, but this project was deleted. Freshwater clams Corbicula and Anodonta have been used successfully to monitor pesticides in rivers and lake stations in the United States according to a report by FAO (1970).

FISH

Trace metals have been studied extensively in fish, and there is an enormous literature on concentrations in many species. Analysis of the data in Volume 2 shows that fish bioaccumulate certain metals to high levels.

Analysis of the use of fish for monitoring environmental gradients of trace metals show that fish have been used to measure gradients of As, Pb and Hg with two or more examples and in one example for Cd and perhaps V. Use of fish for Cu was not significant in three examples. The 15 examples for mercury show that various fish species can be used for monitoring, especially pike.

Phillips (1977) states "the use of telecosts or their tissues as indicators of pollution by trace metals does not at this time seem justifiable, with the exception of studies on mercury. Although metals are known to concentrate preferentially in certain organs, the relationship of organ concentration of metals to the ambient environmental concentration of metals is uncertain and may be affected by several variables." Phillips (1977) states that the use of tissue from fish as an indicator of pollution by trace metals, other than mercury, is open to criticism, and use of muscle tissue has been advised against by investigators in several studies. He also states that no consistent differences were found between concentrations of metals in the muscles of fish from polluted and non-polluted areas, for any fish species, except for mercury.

Concentrations of metals vary with the season, age, size, weight, and feeding habits of the fish, and perhaps from the effects of the toxic pollutants. The factors of age, size and weight can be eliminated by the weight-normalization methods described by Johnels et al. (1967) so that concentrations of mercury from different sites can be compared on the basis of the "standard 1 kg pike." Fish obtain trace metals from food and also from trace elements and compounds in solution. Certain bottom feeding omnivorous fish such as carp probably ingest inorganic and organic sediments.

While fish muscle has been used for measuring mercury, other trace elements such as cadmium and copper occur in highest concentration in soft organs such as liver, kidney, spleen, heart and gonads. Lead and manganese are concentrated in bony tissue such as the gill, backbone and tail (Brooks and Rumsey 1974). Tin in pike muscle was 5.43 ppm and up to 17.0 ppm wet weight (Uthe and Bligh 1971, and Tong et al. 1972).

For estuarine and coastal marine areas, certain demersal non-migratory species such as Platycephalus bassensis has been suggested for monitoring mercury by Dix et al. (1976) and perhaps for cadmium using liver tissue (Phillips 1977).

The use of fish for biological monitoring of the environment appears to be limited to mercury in freshwater and perhaps arsenic, nickel and tin. In the marine environment fish may be used for arsenic and perhaps cadmium and mercury. More research is needed to determine the effects of variables and the relationship of organ concentrations to ambient and environmental gradients of concentrations of trace metals.

Fish are included for surveillance monitoring primarily because they are important food for humans. There are reservations about their use for exposure assessment monitoring, or for monitoring environmental gradients of trace metals except the few trace metals listed above.

SECTION V

BIOLOGICAL MONITORING SYSTEMS AND NETWORKS

The primary objective of this report is to analyze the needs, priorities and objectives for biological monitoring and to select the best biological monitoring organisms. However, it is important to consider how they are used in meeting the objectives. The design of monitoring systems including siting, number of monitoring sites, data collection and analysis, costs and personnel required are outside of the scope of this study.

The use of biological monitoring organisms in integrated exposure assessment monitoring programs, and in the present environmental and food surveillance programs is briefly discussed, with comments on the potential use of new biological monitoring organisms proposed in this report.

INTEGRATED EXPOSURE ASSESSMENT MONITORING PROGRAM

In establishing an integrated exposure assessment monitoring program, guidelines have been developed to provide a systematic and coordinated approach (Behar et al. 1979).

The system design is as follows:

1. Define geographic area of consideration.
2. Identify pollution sources, causes and methods of waste disposal, mass balance studies, exposure routes.
3. Identify potential pollutants.
4. Study existing air, water, and land quality.
5. Define meteorologic and hydrogeologic situations.
6. Identify receptors (especially critical receptors).
7. Identify transport, transformation and fate mechanisms.
8. Set priorities for sources and causes.
9. Establish monitoring approaches -- verify station siting.

10. Establish an adequate quality assurance system to achieve necessary accuracy.

11. Select and implement the monitoring program.

12. Interpret, summarize and transmit the monitoring information (required for efficient control of critical sources).

In selecting biological monitoring organisms and developing biological monitoring systems and networks it is necessary to take into consideration most of the steps of these guidelines and to determine those aspects for which biological monitoring organisms are best suited. An optimum monitoring system should be a combination of integrated physical, chemical and biological measurements.

Traditionally most monitoring program assess only single pathway systems, but in contrast, integrated monitoring attempts to assess total exposure to a pollutant or combination of pollutants (EPA 1976). This requires consideration of monitoring man, the immediate environment of man and those parts of the general environment which relate directly to critical sources, critical pathways and exposure routes.

The biological organisms and tissues recommended for human exposure assessment monitoring include the following:

-- For monitoring man: human hair
-- For monitoring the immediate environment of man: rat, pigeon, domestic animals, food plants, and mosses and lichens
-- For monitoring the environment related to critical sources and critical pathways: This would have to be analyzed carefully and the appropriate organisms would have to be selected depending on trace metals, sources, pathways, media and habitat. Any of the organisms discussed in Section IV could be considered, in addition to many potential biological monitoring organisms listed in Section III.

If the critical sources and/or critical pathways are unknown, it may be necessary to conduct special or temporary research monitoring or specialized surveillance monitoring with biological monitors and instruments to identify the sources, pathways and exposure routes. After identificaiton, integrated exposure assessment monitoring could be established with the prime objective of being able to obtain data to permit control or amelioration of the critical source or sources. It is necesary to have standards to provide guidance to eliminate or reduce the toxic trace metal pollution to safe or acceptable tolerance levels. An analysis of an integrated exposure assessment monitoring model for lead is presented in a report by EPA (1976).

BIOLOGICAL SURVEILLANCE MONITORING OF THE ENVIRONMENT AND FOOD

The objectives of biological surveillance monitoring have been stated in Section IV. Environmental surveillance is reviewed first on the global level, and then on the national level based on the present biological surveillance program of the United States.

Global Environment

It is essential to measure the amount and rate of environmental and biotic changes that are taking place in the world. It is necessary to establish benchmark sites in remote or non-impact areas where baselines for toxic trace metals can be established and monitored on a permanent basis. These benchmark sites should be carefully located to represent all major terrestrial and aquatic biomes of the world. Benchmark monitoring sites are permanent geographic locations where environmental including chemical, physical and biological baselines and their fluctuations can be systematically monitored.

Various analyses and studies by the International Biological Program (Global Network for Environmental Monitoring, GNEM), the SCOPE (Global Environmental Monitoring Systems, GEMS) (SCOPE 1, 1971), and the UNESCO Man and Biosphere (MAB) report on Monitoring and Pollution Research have all considered baseline monitoring stations. There is fairly good agreement on the environmental pollutants to measure, but the actual monitoring programs are in the process of being developed and designed.

A planned pilot project on human biological monitoring by UNEP/WHO (1978) was proposed as part of the UNEP Global Environmental Monitoring System (GEMS). This program proposes to measure cadmium in the kidney cortex from autopsies to estimate lifetime exposure, and blood from living persons to estimate recent exposure. Lead will be measured in blood samples to indicate exposure for the last several weeks. Mercury will be measured in samples of hair and perhaps blood to indicate exposure over the last few months. Organochlorine will be measured in mothers' milk and perhaps in blood. It is planned that 10 to 15 countries will participate in this study.

An earlier study by SCOPE recommended that a GEMS worldwide biological monitoring program as part of EARTHWATCH of UNEP be established using human hair, lichens, and fish muscle to measure lead, cadmium and mercury. These were planned to be analyzed in the EARTHWATCH baseline stations over the world (Jensen and Brown 1976).

The International Atomic Energy Agency (IAEA 1977) has a project "Accelerator-Based Techniques for the Analysis of Pollutants in Human Hair." This program is coordinated with UNEP and WHO and cooperates with laboratories over the world in assisting research and standardizing procedures for monitoring hair.

The Food and Agriculture Organization (FAO 1970, and Portmann 1976) have considered biological monitoring of toxic trace metals in the marine environment, particularly food organisms, on a global, regional, or local scale. A manual was developed to assist in development of the program.

"Mussel Watch" was initiated by Goldberg (1975) as a first step in global marine monitoring. He recommended using Mytilus edulis and similar species in 100 coastal and open ocean sites to monitor halogenated hydrocarbons, transuranics, heavy metals, and petroleum. The mussels would be both indigenous and transported to buoys and other sites.

The first workshop which implemented "Mussel Watch" formally and informally throughout the world's coastal seas, was held at Barcelona, Spain, December 4 through 7, 1978 (Ellis 1979). The planned approach is to use mussels, followed by oysters, as in situ integrators with the following objectives:

1. To locate pollution "hot spots,"
2. To generate regulatory action,
3. To generate studies measuring socio-economic impact,
4. To generate research on cause and effect relationships,
5. To indicate whether insidious long-term toxicant increases are occuring.

Global biological surveillance monitoring is needed for lead, cadmium, and arsenic. Some monitoring is needed for mercury and other toxic trace elements. The best biological monitoring organisms would appear to be: for monitoring human beings -- human hair; for monitoring the atmosphere -- mosses and lichens; for monitoring the marine environment -- Mytilus edulis and oysters combined with marine algae such as Fucus or Ascophyllum. Biological monitoring of freshwater is needed, but there are few proven effective biological monitoring organisms. Bivalve molluscs such as Anodonta and others, and pike for monitoring mercury could be considered. These recommendations do not fully agree with using fish muscle (as recommended in GEMS) as one of the three major biological organisms for global biological monitoring.

National Biological Monitoring (United States)

The Federal Environmental Pesticides Control Act of the United States requires the Environmental Protection Agency (EPA) to prepare a National Pesticide Monitoring Plan, to act on this plan, and carry it out. It attempts to use existing pesticide monitoring networks whenever possible and to integrate national, regional and state programs into a national monitoring network. The objectives of the National Pesticide Monitoring Plan are: 1) To establish national baselines for pesticide residues in identified enviromental components, 2) To establish trends for pesticide residues through time on a national scale, 3) To establish national networks for pesticide effects monitoring, 4) To serve as an early warning system on potential problems, 5) To provide data as a basis for evaluating management and regulatory decisions, 6) To provide the framework for intensive monitoring activities on specific problem areas, 7) To provide framework for meaningful Federal, State and local coordinated monitoring, and 8) To provide for an integrated National Environmental Pesticide Data System.

The ongoing National Pesticide Monitoring Plan is reviewed at intervals by EPA, which has the responsibility to review the following: 1) Assess whether the existing National Pesticide Monitoring program has met its objectives; 2) Determine whether the data collected in these programs can be interrelated; 3) Determine the feasibility of using the data for mathematic modeling and statistical analyses to be used in statements about the movement of pesticides in the environment, and in predictive equations about pesticides in the environment; 4) Make recommendations on ways to improve, modify or upgrade the existing national networks. The scope of this program is broad and covers a large number of pesticides including many chlorinated hydrocarbons and others, so that heavy metals are only one part of the program. It also includes non-biological monitoring of soil, water and air.

The program has national monitoring networks supported by regional, State and local monitoring systems. This is all integrated into the National Environmental Pesticide Monitoring Networks. The present biological monitoring of trace metals in that program is shown in Table 43.

The present study on biological monitoring is restricted to selected trace metals only, and comments are limited to use of biological organisms for monitoring these trace metals based on analysis of needs and priorities for biological monitoring (Table 4). The needs for surveillance of trace metals in the environment 1) on a regional or national level showed lead and cadmium to have highest priority and lower priority for arsenic, mercury, nickel and selenium; 2) on a local level, showed lead, cadmium, arsenic and mercury having highest priority, and lower priority on an as-needed basis, for antimony, beryllium, chromium, cobalt, copper, nickel, selenium, tin and vanadium. Biological monitoring needs for surveillance of trace metals in food include cadmium, lead, mercury and arsenic in that priority, with limited surveillance for cobalt, copper, nickel, selenium and tin in specific foods.

NATIONAL ENVIRONMENTAL PESTICIDE MONITORING NETWORKS (BIOLOGICAL MONITORING)

National Food and Feed Monitoring Network

The food surveillance program on food plants, domestic animals and their products appears to be effective and no changes or modifications are suggested, based on the data and analyses in the present study.

National Human Tissue Monitoring Networks

This program determines baseline levels of chlorinated hydrocarbons in adipose tissue of humans in the continental United States and also determines changes in these levels in time, in 75 metropolitan sites. Consideration is being given to devising a system for monitoring toxic heavy metals in humans.

It is proposed that human hair be used for monitoring lead, cadmium, mercury and arsenic, and other metals if needed. The use of human hair is discussed in Section IV.

TABLE 43. BIOLOGICAL MONITORING OF TRACE METALS IN UNITED STATES NETWORKS

Program	Organisms	Sample Sites	Heavy Metals	Organization or Agency
National Freshwater Fish Monitoring Network	Fish	Freshwater, 100 sites	Hg, Pb, As, Cd, and Se	FWS
National Ocean Monitoring Network	Fish	Atlantic, Gulf, Pacific and Alaska coasts	Hg, Pb, Cd	NOAA and EPA
National Estuarine Monitoring Network	Fish, molluscs and crustacea	113 estuaries	"Heavy Metals"	EPA
National Pesticide Network for Monitoring Birds	Starlings, (odd years) body less wings, beak, skin, legs	51 sites	Hg, Pb, Cd, As, and Se	FWS
National Pesticide Network for Monitoring Birds	Black and Mallard duck wings	48 states	Hg	FWS
National Pesticide Network for Monitoring Birds	Woodcock liver and muscle (1970-1973)	23 eastern and midwestern states	Hg	FWS
National Food and Feed Monitoring Network	Total diet, food plants, preserved foods	30 cities	Hg, As, Cd, Pb, Se and Zn	FDA
National Food and Feed Monitoring Network	Domestic animals, poultry, dairy products	1,200 slaughter houses	Hg, As, Cd, Pb, Se and Zn	USDA
National Small Mammals Monitoring Network	Small mammals (National, proposed)	5 midwest states, 100 sites	"Heavy Metals"	EPA
National Human Tissue Monitoring Network	Human adipose tissue, (hair proposed)	75 areas	chlorinated hydrocarbons, heavy metals proposed	EPA

National Pesticide Monitoring Network for Birds

Duck wings

National surveillance monitoring of mercury in the wings of the mallard duck Anas platyrhynchos and the black duck Anas rubripes was initiated in the 1969-1970 season. Wings from birds shot by hunters were frozen and trimmed by bandsaw to remove the distal joint and most of the feathers, and the remainder was chopped and blended. Wings of about 5,200 ducks pooled by state were analyzed for organochlorines and mercury. Black ducks which were more carnivorous had about twice the mercury level of the more herbivorous mallard ducks. Since black ducks occur in the Eastern United States, levels in the Atlantic flyway were higher. Mercury levels in the mallards in all flyways were comparable. Levels of mercury exceeded 0.5 ppm wet weight in New York, Wisconsin, and Nevada (Heath and Hill 1974).

Black and mallard ducks are highly migratory. The chopped wing is not as suitable as feathers and liver for analyzing mercury. It does not appear that the data obtained can be used to determine trends in levels, compare levels in different geographic areas or fulfill other objectives of monitoring, except surveillance as food for humans. The highly migratory habits of these ducks do not make the use of better tissues such as feathers and liver attractive for monitoring trace metals.

Starlings

The starling Sturnus vulgaris is an introduced species that is found throughout the United States. It is abundant and has been well studied with regard to trace metals. Its value for biological monitoring is decreased because some populations are migratory. This complicates studies of baselines, trends, and comparison of geographic levels of trace metals.

In the starling monitoring program, the body without the feathers, skin, beak, feet and wings is used to measure nationwide residues of mercury, lead, cadmium, arsenic and selenium. Mercury and lead were analyzed in 1970, plus cadmium and arsenic in 1971, plus selenium in 1973. This is part of a national surveillance monitoring program for organochlorine and other pesticides. Results of the program indicate an overall decline in mercury and lead and an increase in arsenic in starlings from 1971 to 1973. Lead was higher in urban than in rural areas (Martin 1972, Martin and Nickerson 1973, and White et al. 1977).

While starlings have been used extensively for environmental surveillance monitoring in the United States, the whole body analysis is not optimal for trace metal analysis. White et al. (1977) state that residues of cadmium would be higher if the major accumulator organs such as kidney or liver were used instead of the whole body. Getz et al. (1977a) found that the best tissues for monitoring lead were feathers and the femur, and that using these tissues, data were highly significant comparing urban and rural birds. However, levels in muscle were low and the differences between urban and rural birds were not statistically significant in this tissue.

It is suggested that the starling monitoring program be reviewed with regard to objectives, because of migration of some populations, and to consider the validity and feasibility of monitoring feathers, kidney, liver, and bone for appropriate trace metals in selected localities.

Eagles

Eagles are not regularly monitored, but dead specimens are analyzed for Pb, Cd, Hg and As and could be included in Table 43.

National Freshwater Fish Monitoring Network

Trace metals have been monitored in freshwater fish in 100 localities in the United States. Mercury was measured in 1969-1973, and lead, cadmium, selenium and arsenic in 1971-1973 according to Henderson et al. (1972) and Walsh et al. (1977). Whole bodies were ground and analyzed. Of fish species that exceeded 0.5 ppm, seven were predatory and five were omnivores or bottom feeders. Species were over 0.5 ppm lead, cadmium, selenium and arsenic levels included various species of non-predatory as well as predatory fish. Species of fish collected, varied considerably between geographic regions, but were similar from year to year within each region. There were no clear trends in changes of levels of these trace metals from 1971 to 1973. Biological monitoring of freshwater fish in this program appears to be well organized with good sampling and analytical techniques, suitable for surveillance of fish for human food.

For biological monitoring of trace metals in the freshwater environment or for exposure assessment monitoring, fish appear to be useful only for mercury and perhaps for arsenic and nickel. The age-size-weight factors must be eliminated by weight normalization (Johnels et al., 1967) e.g. "standard 1 kg pike" before concentrations from different sites can be compared. Whole body comparisons for As, Cd, Pb and Se may not be valid, since even the use of data for trace metals concentrated in specific organs are somewhat questionable for environmental monitoring. The use of fish for monitoring trace metals has been reviewed by Phillips (1977) and the present study. They agree that more critical research appears to be needed before making environmental comparisons except for mercury. Planned biological monitoring of marine fish could include certain edible demersal species (Section IV).

PROPOSED NATIONAL ENVIRONMENTAL PESTICIDE MONITORING NETWORKS

The National Environmental Pesticide Monitoring Networks Program has been reviewed, considering the objectives, needs, priorities, and available biological monitoring organisms presented in this report.

It is recommended that this program establish monitoring networks that will assess the exposure to lead and also to cadmium of humans at highest risk, especially children in cities. Biological monitoring of man can be accomplished using human hair. The immediate environment of man can be monitored using rats and pigeons. Biological monitoring of lead and cadmium in the atmosphere using mosses and lichens has proved highly effective. These are the major recommendations of this report. Other metals such as arsenic and mercury could also be monitored using these biological monitoring organisms.

The proposed program for biological monitoring within the National Environmental Pesticide Monitoring Networks, is presented in Table 44. This includes the above recommended monitoring organisms, the present programs, and suggested modifications to the monitoring network program.

TABLE 44. PROPOSED BIOLOGICAL MONITORING OF TRACE METALS FOR THE NATIONAL ENVIRONMENTAL PESTICIDE MONITORING NETWORKS

Species	Organ or Tissue	Trace Metals	No. Sites	Monitoring Frequency	Status
Human G	hair	Pb,Cd,Hg,As	75 cities	biennial	proposed-new
Rat	hair, liver	Pb,Cd,Hg,As	pilot study, then 75 cities	biennial	proposed-new
Cow, pig, sheep	edible tissue and dairy products	Pb,Cd,Hg,As, Se and An	1,200 slaughter houses	bimonthly	USDA program
Pigeon	feather, liver, kidney	Pb,Cd,Hg,As	pilot study, then 75 cities	biennial	proposed-new
Starling	feather, liver, kidney	Pb,Cd,Hg,As	53	biennial	modified-FWS program
Eagle	feather, liver, kidney	Pb,Cd,Hg,As	dead birds	when available	FWS program
Poultry	edible tissue and eggs	Pb,Cd,As,Hg, Se and Zn	1,200 slaughter houses	bimonthly	USDA program
Food plants	edible parts	Pb,Cd,As,Hg, Se and Zn	35 cities	bimonthly	FDA program

(continued)

TABLE 44. (Continued)

Species	Organ or Tissue	Trace Metals	No. Sites	Monitoring Frequency	Status
Mosses and lichens G	whole plant	Pb, Cd, As, Ni	100 air monitoring sites	quarterly	proposed for EPA-new
Fish, freshwater, few edible species	liver, muscle	Hg, As	50	biennial	modified FWS program
Fish, marine few edible species	muscle, liver	Hg, Pb, Cd	pilot study	biennial	modified FDA and NOAA
Mytilus edulis G	soft parts	12 trace elements	pilot study	annual	"Mussel watch" global-new
Oyster, crab and lobster	edible tissue	Pb, Cd, Hg, As	selected coastal sites	annual	modified FDA, FWS, NOAA

G - part of global surveillance programs of GEMS and "Mussel watch"

SECTION VI

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